Activation and Oxidation of Mesitylene C-H Bonds by (Phebox)Ir(III) Complexes

Meng Zhou,[†] Samantha I. Johnson,[#] Yang Gao,[†] Thomas J. Emge,[†]

Robert J. Nielsen,[‡,] William A. Goddard, III,[‡] Alan S. Goldman[†,]**

[†]Department of Chemistry and Chemical Biology, Rutgers New Brunswick - Busch Campus, 610 Taylor Road, Piscataway, New Jersey 08854, United States

[#]California Institute of Technology, Department of Applied Physics and Materials Science, Pasadena, CA 91125

[‡]California Institute of Technology, Department of Chemistry, Pasadena, CA, 91125, United States

Supporting Information

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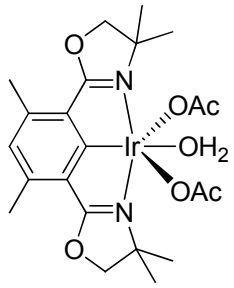
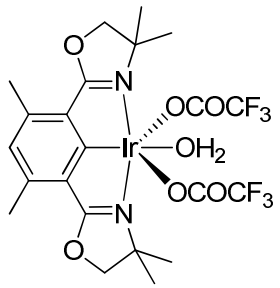
General

Most solvents and reagents were purchased from VWR or Sigma Aldrich, and used without further purification. Extra pure (99%) mesitylene was purchased from Acros Organics. Silver (I) oxide in 99.99% purity was purchased from Alfa Aesar. Silver (I) oxide in 99% purity was purchased from Sigma-Aldrich. Mesitylene-d_{12} was purchased from Cambridge Isotope Laboratories. A MBraun glove box was used to assemble chemicals in a reaction vessel and to store complexes **3** and **4** under argon (<0.1 ppm O_2 and <0.1 ppm H_2O). NMR analyses were performed on 300, 400 or 500 MHz Varian spectrometers, and chemical shifts were referenced to solvent signals. Quantitative ^{1}H NMR integrations were performed using a solution of MeCN (20 μL, 64 mM) or 1,3,5-trichlorobenzene (15 mg, 14 mM) in C_6D_6 (6 mL). Parafilm was purchased from VWR. HT-110 oil (flashing point > 288 ^{o}C), produced by Clearco Products, was used for heating at 180 ^{o}C. Silica gel (230-400 mesh) for flash column chromatography was purchased from SiliCycle. Celite (545) was purchased from EMD Chemicals. Regular (5 mm diameter) and medium pressure (maximum pressure: 150 psi) J-Young nmr tubes were purchased from Sigma Aldrich. Reusable culture tubes (50 mL), equipped with PTFE-faced black phenolic caps, were manufactured by Kimax or Pyrex. Maximum safety precaution was applied when handling argon under 120 psi in a medium pressure J-Young NMR tube (see page 9 of this document for details, under section *Excess deuterated acids as source of deuterium*).

Syntheses and characterizations of (Phebox)Ir complexes



*(Phebox)Ir(OCOCH$_3$)$_2$(OH$_2$) (**1**)* was prepared by literature procedures,[1] starting from commercially available 1,5-bis(chloromethyl)-2,4-dimethylbenzene purchased from Sigma-Aldrich. To ensure high product yield, air has been rigorously removed by three cycles of freeze-pump-thaw treatment for all reactions containing iridium.



*(Phebox)Ir(OCOCF$_3$)$_2$(OH$_2$) (**2**)* was prepared in one step from (Phebox)Ir(Cl)$_2$(OH$_2$)$_2$ (a known complex[1]) using silver (I) trifluoroacetate. (Phebox)Ir(Cl)$_2$OH$_2$ (100 mg, 172 μmol) and two equivalents of silver (I) trifluoroacetate (344 μmol, 76 mg) were added to a round-bottom flask with dichloromethane solvent (10 mL). Three cycles of freeze-pump-thaw treatment were performed to remove air, and argon was introduced to the flask at one atmosphere pressure. The reaction mixture was stirred at room temperature for 20 hours. At the end of reaction, the solution was filtered through celite in air and concentrated under vacuum. Silica gel flash column chromatography (1:4 ethylacetate/hexane) was performed to yield complex **2** in 76% yield. The product can be further purified by recrystallization in dichloromethane/hexane.

Single crystal for x-ray structure determination was obtained by evaporation over two days using a solution of **2**, in a mixture of dichloromethane, hexane and a small amount of methanol, under air at room temperature. See Supporting Information II in a separate document for details of x-ray structure determination.

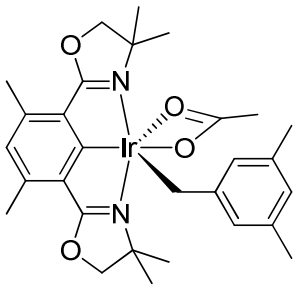
NMR Spectroscopy: $^{1}H\{^{13}C\}$ NMR chemical shifts (in C_6D_6 and referenced at 7.16 ppm): 6.29 ppm (1H, Ar-H, s), 3.76 ppm (4H, CH_2O, s), 2.36 ppm (6H, benzylic CH_3, s), 1.16 ppm (12H, aliphatic CH_3, s).

$^{1}H\{^{13}C\}$ NMR chemical shifts (in $CDCl_3$ and referenced at 7.26 ppm): 6.71 ppm (1H, Ar-H, s), 4.62 ppm (4H, CH_2O, s), 2.68 ppm (6H, benzylic CH_3, s), 1.43 ppm (12H, aliphatic CH_3, s).

$^{1}H\{^{13}C\}$ NMR chemical shifts (in CD_3OD and referenced at 3.31 ppm): 6.69 ppm (1H, Ar-H, s), 4.70 ppm (4H, CH_2O, s), 2.65 ppm (6H, benzylic CH_3, s), 1.46 ppm (12H, aliphatic CH_3, s).

$^{13}C\{^{1}H\}$ NMR chemical shifts (in CD_3OD and CD_3OD referenced at 49 ppm): 18.77 ppm (s), 26.87 ppm (s), 65.97 ppm (s), 83.31 ppm (s), 113.6 ppm (q, J = 290 hz, $OCOCF_3$), 127.2 ppm (s), 128.9 ppm (s), 141.5 ppm (s), 165.4 ppm (d, J = 37.7 hz, Ir-C), 166.3 ppm (s), 179.4 ppm (s).

$^{19}F\{^{13}C\}$ (in C_6D_6 and with C_6F_6 referenced at -163.3 ppm) NMR chemical shifts: -75.3 ppm ($OCOCF_3$, s).



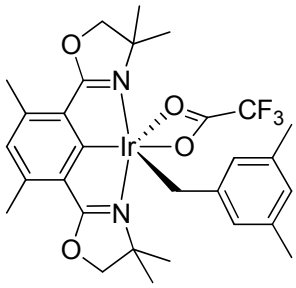
*(Phebox)Ir(mesityl)($OCOCH_3$) (**3**)* was made in one step from complex **1** using mesitylene under argon. Complex **1** (2 mg, 3.2 μmol, 10.6 mM), mesitylene (300 μL, 7.19M) and K_2CO_3 (4 equivalents, 1.8 mg, 42.4 mM) were added to a 5 mm outer diameter J-Young NMR tube, in a glove box under argon. The tube was then taken out of the glove box and heated in an oil bath at 130 ^{o}C for 12 hours. At the end of reaction, mesitylene solvent was removed under vacuum. Ether dissolved complex **3** and the solution was filtered through a pipette packed with a glass wool plug. Complex **3** was obtained in >90% yield by $^{1}H\{^{13}C\}$ NMR analysis in C_6D_6 using MeCN (64 mM) as internal standard. Product can be further purified by recrystallization in ether/pentane, at -32 ^{o}C and in a glove box.

Complex **3** in solid state appeared to be stable under argon for at least two weeks. Preparation in large scale (40 mg complex **1**, 64 μmol, 10.6 mM and mesitylene in 6 mL, 7.19 M) was performed in a 50 mL flask equipped with Kontes valve without stirring. Reaction time of up to 20 hours were applied to ensure reaction to reach completion

Single crystal for x-ray structure determination was obtained by slow evaporation (with significant amount of liquid still remaining) using a solution of complex **3** in pentane, at -32 ^{o}C, under argon and inside a glove box. Single crystal for x-ray structure determination was also obtained in another case by slow evaporation to dryness over a day using a solution of **3** in C_6D_6. Cooling the solution containing **3** to -32 ^{o}C in a glove box can facilitate recrystallization. See Supporting Information II in a separate document for details of x-ray structure determination.

NMR Spectroscopy: $^{1}H\{^{13}C\}$ NMR chemical shifts (in C_6D_6 and referenced at 7.16 ppm): 6.67 ppm (1H, ligand Ar-H, s), 6.53 ppm (1H, mesityl Ar-H, s), 6.30 ppm (2H, mesityl Ar-H, s), 3.81 ppm (2H, CH_2O, d, J = 8.1 Hz), 3.65 ppm (2H, CH_2O, d, J = 8.1 Hz), 2.86 ppm (2H, Ir-CH_2-Ar, s), 2.67 ppm (6H, phebox ligand benzylic CH_3, s), 2.16 ppm (6H, mesityl benzylic CH_3, s), 2.04 ppm (3H, $OCOCH_3$, s), 1.29 ppm (6H, two aliphatic CH_3, s), 1.20 ppm (6H, two aliphatic CH_3, s).

$^{13}C\{^{1}H\}$ NMR chemical shifts (C_6D_6 at 128.6 ppm): -1.43 ppm (s, Ir-CH_2), 19.50 ppm (s), 21.83 ppm (s), 25.93 ppm (s), 26.44 ppm (s), 28.06 ppm (s), 66.45 ppm (s), 82.52 ppm (s), 123.6 ppm (s), 125.1 ppm (s), 127.1 ppm (s), 127.3 ppm (s), 136.4 ppm (s), 140.0 ppm (s), 150.5 ppm (s), 177.6 ppm (s), 182.4 ppm (s), 185.9 ppm (s)



*(Phebox)Ir(mesityl)($OCOCF_3$) (**4**)* was made in one step from complex **3** under argon. Complex **3** (2.1 mg, 3.2 μmol, 10.6 mM), trifluoroacetic acid (1.1 equivalent 3.5 μmol, delivered in 80 μL of trifluoroacetic acid stock solution in mesitylene, concentration: 43.6 mM) and mesitylene solvent (220 μL, 7.19 M) were added to a 5 mm O.D. J-Young NMR tube in a glove box. The tube was then taken out of glove box and was shaken to ensure that all complex **3** dissolved. After 1 hour at room temperature, excess amount of K_2CO_3 was added under argon to the solution mixture to neutralize acetic acid side product. Mesitylene solvent was removed under vacuum. Pentane and ether dissolved complex **4** and the solution obtained was filtered by glass wool through a pipette in a glove box. The product was obtained in >90% yield by ^{1}H NMR analysis. Further purification was performed by recrystallization in ether/pentane in a glovebox at -32 ^{o}C.

$^{1}H\{^{13}C\}$ NMR chemical shifts (in C_6D_6 and referenced at 7.16 ppm): 6.64 ppm (1H, ligand Ar-H, s), 6.49 ppm (1H, mesityl Ar-H, s), 6.27 ppm (2H, mesityl Ar-H, s), 3.78 ppm (2H, CH_2O, d, J = 8.3 Hz), 3.58 ppm (2H, CH_2O, d, J = 8.2 Hz), 3.03 ppm (2H, Ir-CH_2-Ar, s), 2.61 ppm (6H, Phebox ligand benzylic CH_3, s), 2.13 ppm (6H, mesityl benzylic CH_3, s), 1.16 ppm (6H, two aliphatic CH_3, s), 1.08 ppm (6H, two aliphatic CH_3, s).

$^{19}F\{^{13}C\}$ (in C_6D_6 and with C_6F_6 referenced at -163.3 ppm) NMR chemical shifts: -75.5 ppm (s).

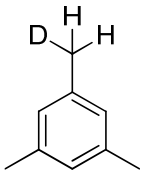
$^{13}C\{^{1}H\}$ NMR chemical shifts (C_6D_6 at 128.6 ppm): -3.19 ppm (s, Ir-CH_2), 19.34 ppm (s), 25.92 ppm (s), 28.02 ppm (s), 30.77 ppm (s), 66.57 ppm (s), 82.45 ppm (s), 124.6 ppm (s), 125.6

ppm (s), 127.2 ppm (s), 127.4 ppm (s), 136.7 ppm (s), 140.5 ppm (s), 149.5 ppm (s), 177.9 ppm (s), 178.1 ppm (s).

Single crystal for x-ray structure determination was obtained by slow evaporation over one day of a solution of **4** in hexane, in a 1 mL vial, under argon and in a glove box.

Catalytic H/D exchange using complexes 1 and 2

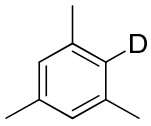
$^{2}D\{^{13}C\}$ NMR of 1-(deuteriomethyl)-3,5-dimethylbenzene and 1,3,5-trimethyl-2-deuteriobenzene



$^{2}D\{^{13}C\}$ NMR of 1-(deuteriomethyl)-3,5-dimethylbenzene when using d_4-acetic acid and complex **1** in h_{12}-mesitylene (using -CD_3 of CD_3CN as reference at 0.6 ppm): 1.92 ppm (t, J = 2.2 hz). The triplet was consistent with deuterium peak being split by two germinal hydrogen atoms.

$^{2}D\{^{13}C\}$ NMR of 1-(deuteriomethyl)-3,5-dimethylbenzene when using d_1-trifluoroacetic acid and complex **2** in h_{12}-mesitylene (using -CD_3 of CD_3CN as reference at 0.6 ppm): 2.06 ppm (t, J = 2.2 hz). The triplet was consistent with deuterium peak being split by two germinal hydrogen atoms.

$^{2}D\{^{13}C\}$ NMR of 1-(deuteriomethyl)-3,5-dimethylbenzene when using D_2O as source of deuterium in h_{12}-mesitylene solvent (using C_6D_6 as reference at 7.16 ppm): 2.14 ppm (broadened triplet, J = 2.1 hz).



$^{2}D\{^{13}C\}$ NMR of 1,3,5-trimethyl-2-deuteriobenzene when using d_1-trifluoroacetic acid and complex **2** in h_{12}-mesitylene (using -CD_3 of CD_3CN as reference at 0.6 ppm): 6.58 ppm (s).

Deuterated acids as source of deuterium

Mesitylene (99% pure, 300 μL), complex **1** or **2** (2.4 mg, 10.6 mM) and d_4-acetic acid or d_1-trifluoroacetic acid (320 μmol, 1.06 M) were added to a 5 mm outer diameter medium pressure J-Young NMR tube, in a glove box under 1 atm argon. The tube with valve closed was then taken out of the glove box and vigorously shaken to ensure proper mixing. Direct analysis by $^{2}D\{^{13}C\}$ NMR spectroscopy using a Varian 500 MHz NMR spectrometer was then performed to

obtain results of the first stage of reaction (entries 1 and 4 in Table 1 of main text). Purchased d_{12}-mesitylene was used to identify ^{2}D NMR chemical shifts of 1-(deuteriomethyl)-3,5-dimethylbenzene and 1,3,5-trimethyl-2-deuteriobenzene. CD_3CN diluted in h_{12}-mesitylene was used as internal standard (0.306 mmol, 51 mM CD_3CN in mesitylene 6 mL), referenced at 0.6 ppm.

An d_{12}-mesitylene sample was used to obtain optimum shimming parameters. The sample was then removed from the spectrometer and the NMR tube containing H/D exchange reaction mixture was analyzed without locking (auto-lock was prohibited by the Vnmrj command, alock='n').

Next the tube was heated in an oil bath for 12 hours at 130 ^{o}C. It was analyzed directly by ^{2}D{^{13}C} NMR spectroscopy to obtain results of the second stage of reaction (entries 2 and 5 in Table 1 of main text). In the final stage of reaction (entries 3 and 6 in Table 1 of main text), the tube was heated for additional 48 hours at 180 ^{o}C. At the end of reaction in stage 3, 400 μL of diluted CD_3CN solution (51 mM CD_3CN in h_{12}-mesitylene) was added to the reaction mixture in a glove box for quantitation by ^{2}D{^{13}C} NMR spectroscopy.

Control experiments of H/D exchange carried out by deuterated acids without Ir

Results of control experiments for each entry of Table 1 of main text were summarized below in Table S1. They were performed in the same way as catalytic H/D exchange except no Ir complex was used.

entry[a]	deuterated acid	time	temperature	1-(deuteriomethyl)-3,5-dimethylbenzene concentration[c]	1,3,5-trimethyl-2-deuteriobenzene concentration[c]
1	$DOCOCD_3$	15min	23 °C	<10 mM	<10 mM
2	$DOCOCD_3$	additional 12h	130 °C	<10 mM	<10 mM
3	$DOCOCD_3$	additional 48h	180 °C	<10 mM	<10 mM
4	$DOCOCF_3$	15min	23 °C	<10 mM	<10 mM
5[b]	$DOCOCF_3$	additional 12h	130 °C	<10 mM	1.06 M
6[b]	$DOCOCF_3$	additional 48h	180 °C	<10 mM	1.06 M

[a]Reaction conditions: no Ir complex present, d_4-acetic acid 1.06 M (100 equivalents) for entries 1 to 3 and d_1-trifluoroacetic acid 1.06 M (100 equivalents) for entries 4 to 6, mesitylene 7.19 M, 300 μL; in a medium pressure, 5 mm outer diameter J-Young NMR tube under 1 atm argon with <0.5 ppm H_2O or O_2 [b]only 1,3,5-trimethyl-2-deuteriobenzene signal; [c]detection limit: 10 mM.

Table S1. Background H/D exchange between deuterated acids and mesitylene in the absence of Ir

Excess deuterated acids as source of deuterium

Mesitylene (99% pure, 50 μL, 0.36 mmol, 1.2 M), complex **2** (2.4 mg, 10.6 mM) and d_1-trifluoroacetic acid (10.8 M, 3.24 mmol) were added to a 5 mm outer diameter medium pressure J-Young NMR tube, in a glove box under 1 atm argon. The tube with valve closed was then taken out of the glove box and vigorously shaken to ensure proper mixing. The medium pressure J-Young NMR tube was then pressurized with 120 psi of argon. The additional argon was used to raise the boiling point of d_1-trifluoroacetic acid and mesitylene.

Maximum safety precaution was taken when using argon under 120 psi. Facial splash shield and eye shield were worn by the investigator when pressurizing medium pressure J-Young NMR tube at room temperature (see Figure S1 for the setup). Teflon tape was applied to wrap the metal connecter to ensure sealing between J-Young valve and the metal connecter. When submerging the J-Young NMR tube to an oil bath at 180 °C, a large benchtop splash shield was placed between the oil bath and the investigator, who was wearing both a facial splash shield and an eye shield. The benchtop splash shield stayed for the entire duration of the experiment. Heating of the medium pressure J-Young NMR tube was and must be performed inside a fume hood.

No accident or harm of any kind occurred in our experiments. However an investigator should consider fail-safe procedures when handling pressurized J-Young NMR tube, so that no harm could be done to anyone even if an accident were to occur.

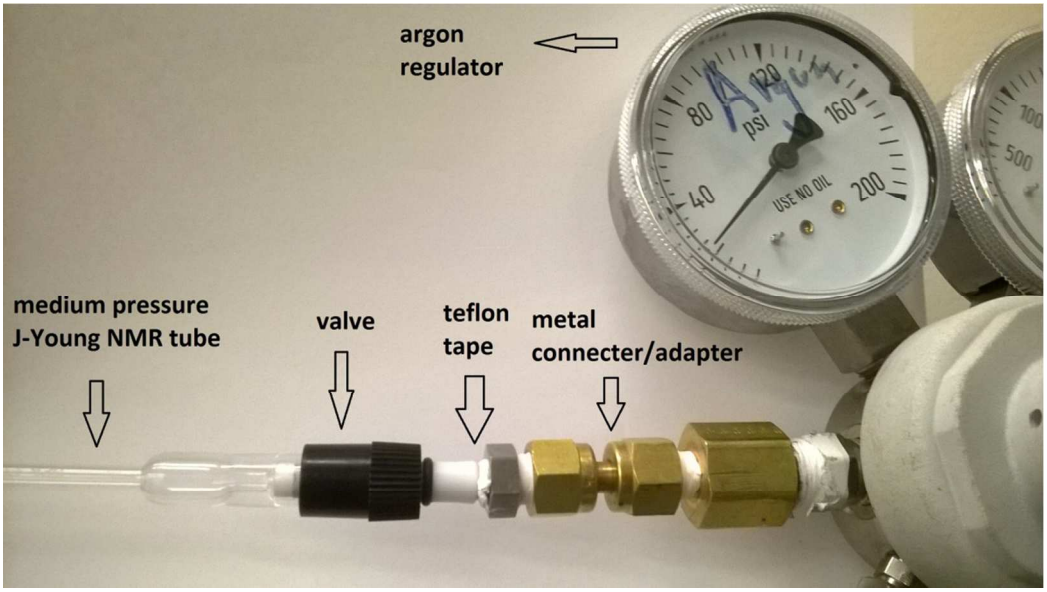


Figure S1. Setup for pressurizing medium pressure J-Young NMR tube

The pressurized J-Young NMR tube was heated at 180 ^{o}C for 12 hours. The reaction vessel was cooled under air to room temperature. Aryl deuterium was detected in 2.32 M. Since mesitylene was present in only 1.3 M, the 2.32 M of aryl deuterium suggested that double deuteration product, 1,3,5-trimethyl-2,4-dideuteriobenzene, could be produced. 1-(deuteriomethyl)-3,5-dimethylbenzene was detected in 177 mM.

However without complex **2** but under otherwise identical conditions 1-(deuteriomethyl)-3,5-dimethylbenzene was also produced in 138 mM along with 1,3,5-trimethyl-2,4-dideuteriobenzene. D_1-trifluoroacetic acid when used in high concentration (10.8 M) was capable of carrying out benzylic H/D exchange without Ir. The 138 mM of 1-(deuteriomethyl)-3,5-dimethylbenzene produced by d_1-trifluoroacetic acid alone did not differ much from the 177 mM of 1-(deuteriomethyl)-3,5-dimethylbenzene produced using complex **2**.

D_2O as source of deuterium

Mesitylene (99% pure, 300 μL), complex **1** or **2** (2.4 mg, 10.6 mM) and D_2O (1.11 mmol, 3.68 M) were added to a 5 mm outer diameter medium pressure J-Young NMR tube under air. Freeze-pump-thaw treatment of the reaction mixture was performed three times to remove air. The medium pressure J-Young NMR tube was then pressurized with 120 psi of argon. The tube

was then vigorously shaken to ensure proper mixing. The tube was heated in an oil bath for 12 hours under 180 ^{o}C.

At the end of reaction 100 μL of a solution (concentration of C_6D_6: 225 mM) of C_6D_6 (20 μL) in h_{12}-mesitylene (1 mL) was added to the reaction mixture as internal standard for quantitative $^{2}D\{^{13}C\}$ NMR analysis.

Oxidation of mesitylene catalyzed by complexes 1 and 2

Mesitylene (99% pure, 300 μL), complex **2** (2.4 mg, 10.6 mM) and Ag_2O (99.99% pure, 40 equiv., 128 μmol, 424 mM, 30 mg) were added to a J-Young NMR tube, in a glove box under 1 atm argon. The tube with valve closed was then taken out of the glove box and heated in an oil bath for 12 hours at 130 ^{o}C.

Silver mirror coated on the glass wall was observed at the end of reaction. Mesitylene was removed under vacuum and the tube was taken into a glove box, where a solution of MeCN (64 mM) in C_6D_6 (300 μL) was added to dissolve the product mixture for $^{1}H\{^{13}C\}$ NMR analysis, using the MeCN singlet at 0.604 ppm for quantitation. The product identities were verified by comparing with the $^{1}H\{^{13}C\}$ and $^{13}C\{^{1}H\}$ NMR spectra of purchased samples dissolved in C_6D_6.

Recovered complex **2** at the end of catalytic oxidation (entries 1 and 2 in Table 3 of the main text) was measured using an internal standard MeCN. We found that the $^{1}H\{^{13}C\}$ NMR peaks of complex **2** were shifted when MeCN was present. It was possible that complex 2 undertook facile ligand exchange from OH_2 to MeCN, to form (Phebox)Ir$(OCOCF_3)_2$(NCMe).

Oxidation of (Phebox)Ir complexes by one equivalent of Ag_2O

*Oxidation of complexes **3** and **4***

Mesitylene in 300 μL (7.19M), complex **3** or **4** (6.4 μmol, 21.2 mM) and 1 equiv. of Ag_2O (6.4 μmol, 21.2 mM, 1.4 mg, 99.99% pure) were added to a J-Young NMR tube, in a glove box under argon. NaOAc (21.2 mM, 6.4 μmol) or $NaOCOCF_3$ (21.2 mM, 6.4 μmol) was added in the case of entries 2 and 4 in Table 4. The tube with the valve closed was then taken out of the glove box and heated at 130 ^{o}C in an oil bath for 12 hours. At the end of reaction, the tube was cooled under air. Mesitylene solvent was removed under vacuum at 23 ^{o}C. The tube was then transferred to the glove box, where a stock solution (300 μL) of MeCN in C_6D_6 (stock solution: MeCN 64 mM in C_6D_6) was transferred to the tube for quantitative $^{1}H\{^{13}C\}$ NMR analysis.

*Oxidation of complexes **1** and **2***

Mesitylene in 300 μL (7.19 M) or C_6F_6 in 300 μL (8.7 M), complex **1** or **2** (3.2 μmol, 10.6 mM) and 1 equiv. of Ag_2O (3.2 μmol, 10.6 mM, 0.7 mg, 99.99% pure) were added to a J-Young NMR tube, in a glove box under argon. The tube with the valve closed was then taken out of glove box and heated at 130 ^oC in an oil bath for 12 hours. At the end of reaction, the tube was cooled under air. Mesitylene solvent was removed under vacuum at 23 ^oC. The tube was then transferred to the glove box, where a stock solution of MeCN in C_6D_6 (300 μL) (stock solution: MeCN 64 mM in C_6D_6) was transferred to the tube for $^1H\{^{13}C\}$ NMR analysis.

Results are summarized in Table S2. For entries 1, 2 and 4 we could not isolate and characterize the mixture of new species formed at the end of reaction due to their low yield (<10% in total). However the oxidation of complex **1** in C_6F_6 appeared to produce only one new species in 14% yield. We were unable to isolate and characterize this new species. Small amount (<10 mM) of 3,5-dimethylbenzaldehyde and 3,5-dimethylbenzoic acid formed when using mesitylene solvent in entries 1 and 3 of Table S2.

entry[a]	**complex**	**solvent**	**recovered Ir complex**[b]	**$^1H\{^{13}C\}$NMR analysis**[c]
1	**1**	mesitylene	15%	65% yield of complex **3** and new species (<10% yield)
2	**1**	**C_6F_6**	**80%**	**one new species in 14% yield**
3	**2**	mesitylene	69%	new species (<10% yield)
4	**2**	C_6F_6	79%	new species (<10% yield)

[a]Reaction conditions: complex **1** or **2** (3.2 μmol, 10.6 mM), mesitylene solvent in 7.19 M or C_6F_6 solvent in 8.7 M, at 130 ^oC for 12 hours; 300 μL; in a medium pressure, 5 mm outer diameter J-Young NMR tube under 1 atm argon with <0.5 ppm H_2O or O_2 [b]only 1,3,5-trimethyl-2-deuteriobenzene signal; [c]yield was based on concentration of complex **1** or **2**, 10.6 mM

Table S2. Oxidation of complexes **1** and **2** by one equivalent of Ag_2O

General information for X-ray structure determination

Single-crystal X-ray diffraction data were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo Ka radiation (l = 0.71073Å) at 100 K. The crystals were immersed in oil and placed on a glass needle in the cold stream. The data were corrected for Lorenz effects, polarization, and absorption, the latter by a multi-scan method using program SAINT.[3] The structures were solved by direct methods using program SHELXS.[4] Using program SHELXL,[5] all non-hydrogen atoms were refined based upon Fobs[4] and all hydrogen atom coordinates were calculated with idealized geometries.

1. (Phebox)Ir($OCOCF_3$)$_2OH_2$ **(2)**

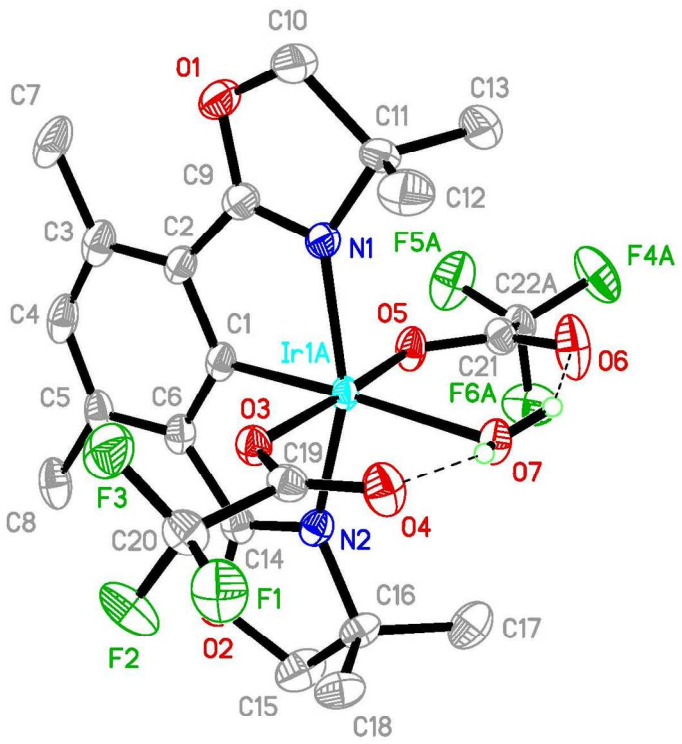


Table S3. Crystal data and structure refinement for IrNONO_COOCF3.

Identification code	IrNONO_COOCF3	
Empirical formula	C22 H25 F6 Ir N2 O7	
Formula weight	735.64	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1482(13) Å	α= 97.296(3)°.
	b = 10.3381(15) Å	β= 107.210(3)°.
	c = 14.352(2) Å	γ = 99.526(3)°.
Volume	1256.1(3) $Å^3$	
Z	2	
Density (calculated)	1.945 Mg/m^3	

Absorption coefficient	5.405 mm^{-1}
F(000)	716
Crystal size	0.240 x 0.210 x 0.090 mm^3
Theta range for data collection	1.512 to 31.247°.
Index ranges	-13<=h<=13, -15<=k<=15, -20<=l<=20
Reflections collected	16614
Independent reflections	8077 [R(int) = 0.0243]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7464 and 0.6256
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8077 / 369 / 520
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	R1 = 0.0254, wR2 = 0.0584
R indices (all data)	R1 = 0.0294, wR2 = 0.0597
Extinction coefficient	n/a
Largest diff. peak and hole	1.912 and -0.519 e.$Å^{-3}$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for IrNONO_COOCF3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1A)	4508(1)	2524(1)	2737(1)	18(1)
O(1)	1971(3)	4252(2)	556(2)	35(1)
O(2)	7750(3)	379(2)	2357(2)	30(1)
O(3)	2810(2)	791(2)	2194(2)	22(1)
O(4)	1781(9)	627(5)	3441(3)	31(1)
O(5)	6307(2)	4177(2)	3144(2)	26(1)
O(6)	6222(3)	5082(3)	4621(2)	42(1)
O(7)	4193(3)	2662(2)	4219(2)	26(1)
N(1)	2942(3)	3562(2)	1989(2)	24(1)
N(2)	6174(3)	1392(2)	2988(2)	22(1)
C(1)	4879(3)	2344(3)	1470(2)	22(1)
C(2)	4064(4)	2964(3)	733(2)	25(1)
C(3)	4378(4)	2894(3)	-169(2)	32(1)
C(4)	5498(4)	2172(3)	-280(2)	33(1)
C(5)	6330(4)	1525(3)	438(2)	28(1)
C(6)	6007(3)	1640(3)	1338(2)	23(1)
C(7)	3566(5)	3550(4)	-988(2)	41(1)
C(8)	7492(4)	749(3)	237(3)	35(1)
C(9)	2977(4)	3608(3)	1095(2)	26(1)
C(10)	978(4)	4573(4)	1144(3)	38(1)
C(11)	1791(4)	4324(3)	2200(2)	28(1)
C(12)	655(4)	3486(4)	2589(3)	39(1)
C(13)	2676(5)	5612(3)	2936(3)	38(1)
C(14)	6662(3)	1123(3)	2237(2)	24(1)
C(15)	8186(4)	245(4)	3405(3)	38(1)
C(16)	6908(3)	688(3)	3789(2)	26(1)
C(17)	7595(4)	1639(4)	4782(3)	37(1)
C(18)	5681(4)	-485(3)	3815(3)	32(1)
F(1)	149(3)	-1776(2)	2521(2)	38(1)
F(2)	1884(2)	-1912(2)	1807(2)	40(1)
F(3)	-42(3)	-1027(2)	1172(2)	40(1)

C(19)	1932(4)	247(3)	2638(2)	22(1)
C(20)	957(3)	-1124(3)	2027(2)	26(1)
C(21)	6723(3)	5033(3)	3935(2)	23(1)
C(22A)	8283(7)	6001(6)	4088(5)	26(2)
F(4A)	8391(11)	7174(7)	4646(7)	47(2)
F(5A)	8499(7)	6274(7)	3252(4)	51(1)
F(6A)	9497(4)	5508(5)	4552(4)	47(1)
C(22B)	7948(8)	6232(7)	3936(5)	31(2)
F(4B)	8594(11)	7021(8)	4828(5)	44(2)
F(5B)	9100(6)	5881(7)	3656(6)	57(2)
F(6B)	7298(8)	6991(6)	3317(5)	62(2)
Ir(1B)	4099(5)	2679(3)	2600(2)	44(1)
O(101)	1320(30)	4630(30)	744(17)	44(1)
O(102)	7290(30)	690(30)	1858(17)	44(1)
O(103)	2410(20)	940(15)	2059(14)	44(1)
O(104)	1810(120)	510(70)	3430(30)	44(1)
O(105)	5910(20)	4317(16)	2986(14)	44(1)
O(106)	5800(40)	5410(30)	4380(20)	44(1)
O(107)	4059(15)	2630(10)	4133(7)	44(1)
N(101)	2460(20)	3750(20)	2036(11)	44(1)
N(102)	5770(20)	1540(20)	2656(12)	44(1)
C(101)	4280(20)	2630(20)	1283(9)	44(1)
C(102)	3370(40)	3330(40)	657(16)	44(1)
C(103)	3580(40)	3420(40)	-265(17)	44(1)
C(104)	4710(40)	2790(40)	-480(20)	44(1)
C(105)	5610(40)	2040(40)	111(19)	44(1)
C(106)	5360(40)	1970(40)	1027(16)	44(1)
C(107)	2650(40)	4170(40)	-960(20)	44(1)
C(108)	6840(40)	1460(40)	-190(20)	44(1)
C(109)	2350(40)	3900(40)	1134(16)	44(1)
C(110)	360(30)	4720(40)	1390(19)	44(1)
C(111)	1340(20)	4410(20)	2389(14)	44(1)
C(112)	350(40)	3450(40)	2800(30)	44(1)
C(113)	2260(40)	5660(30)	3160(20)	44(1)
C(114)	6190(40)	1410(40)	1865(17)	44(1)
C(115)	7710(40)	280(30)	2823(19)	44(1)

C(116)	6720(20)	870(20)	3402(13)	44(1)
C(117)	7750(40)	1840(40)	4340(19)	44(1)
C(118)	5620(40)	-230(30)	3640(30)	44(1)
F(101)	-380(30)	-1520(20)	2290(20)	44(1)
F(102)	1420(30)	-1960(30)	1680(30)	44(1)
F(103)	-90(40)	-740(30)	1010(20)	44(1)
C(119)	1830(50)	230(30)	2576(19)	44(1)
C(120)	660(30)	-1012(19)	1880(18)	44(1)
C(121)	6490(30)	5120(30)	3807(19)	44(1)
C(122)	7690(40)	6310(30)	3740(30)	44(1)
F(104)	8410(80)	7120(50)	4620(40)	44(1)
F(105)	8800(50)	5920(60)	3420(60)	44(1)
F(106)	7010(70)	7050(50)	3110(50)	44(1)
C(222)	8020(30)	6130(30)	3980(30)	44(1)
F(204)	8320(70)	7110(50)	4750(40)	44(1)
F(205)	7990(60)	6700(50)	3200(40)	44(1)
F(206)	9260(30)	5560(60)	4160(50)	44(1)

Table S5. Bond lengths [Å] and angles [°] for IrNONO_COOCF3.

Ir(1A)-C(1)	1.937(3)	C(8)-H(8A)	0.9800
Ir(1A)-N(2)	2.047(2)	C(8)-H(8B)	0.9800
Ir(1A)-O(5)	2.0540(19)	C(8)-H(8C)	0.9800
Ir(1A)-O(3)	2.0587(19)	C(10)-C(11)	1.553(4)
Ir(1A)-N(1)	2.061(2)	C(10)-H(10A)	0.9900
Ir(1A)-O(7)	2.220(2)	C(10)-H(10B)	0.9900
O(1)-C(9)	1.342(4)	C(11)-C(12)	1.520(5)
O(1)-C(10)	1.459(5)	C(11)-C(13)	1.524(4)
O(2)-C(14)	1.341(4)	C(12)-H(12A)	0.9800
O(2)-C(15)	1.468(4)	C(12)-H(12B)	0.9800
O(3)-C(19)	1.269(3)	C(12)-H(12C)	0.9800
O(4)-C(19)	1.224(3)	C(13)-H(13A)	0.9800
O(5)-C(21)	1.262(3)	C(13)-H(13B)	0.9800
O(6)-C(21)	1.202(3)	C(13)-H(13C)	0.9800
O(7)-H(71)	0.855(10)	C(15)-C(16)	1.540(4)
O(7)-H(72)	0.852(10)	C(15)-H(15A)	0.9900
N(1)-C(9)	1.300(4)	C(15)-H(15B)	0.9900
N(1)-C(11)	1.491(4)	C(16)-C(17)	1.517(5)
N(2)-C(14)	1.300(4)	C(16)-C(18)	1.523(4)
N(2)-C(16)	1.489(4)	C(17)-H(17A)	0.9800
C(1)-C(2)	1.396(4)	C(17)-H(17B)	0.9800
C(1)-C(6)	1.401(4)	C(17)-H(17C)	0.9800
C(2)-C(3)	1.403(4)	C(18)-H(18A)	0.9800
C(2)-C(9)	1.462(4)	C(18)-H(18B)	0.9800
C(3)-C(4)	1.397(5)	C(18)-H(18C)	0.9800
C(3)-C(7)	1.498(5)	F(1)-C(20)	1.331(3)
C(4)-C(5)	1.404(5)	F(2)-C(20)	1.343(3)
C(4)-H(4)	0.9500	F(3)-C(20)	1.321(4)
C(5)-C(6)	1.403(4)	C(19)-C(20)	1.542(4)
C(5)-C(8)	1.503(5)	C(21)-C(22A)	1.540(6)
C(6)-C(14)	1.461(4)	C(22A)-F(5A)	1.330(6)
C(7)-H(7A)	0.9800	C(22A)-F(6A)	1.332(6)
C(7)-H(7B)	0.9800	C(22A)-F(4A)	1.337(6)
C(7)-H(7C)	0.9800	C(22B)-F(5B)	1.320(6)

C(22B)-F(6B)	1.334(6)	C(108)-H(10F)	0.9800
C(22B)-F(4B)	1.334(6)	C(108)-H(10G)	0.9800
Ir(1B)-C(101)	1.940(8)	C(108)-H(10H)	0.9800
Ir(1B)-N(101)	2.046(8)	C(110)-C(111)	1.554(10)
Ir(1B)-O(105)	2.051(8)	C(110)-H(11A)	0.9900
Ir(1B)-O(103)	2.058(8)	C(110)-H(11B)	0.9900
Ir(1B)-N(102)	2.069(8)	C(111)-C(112)	1.517(10)
Ir(1B)-O(107)	2.218(8)	C(111)-C(113)	1.524(10)
O(101)-C(109)	1.341(10)	C(112)-H(11C)	0.9800
O(101)-C(110)	1.463(11)	C(112)-H(11D)	0.9800
O(102)-C(114)	1.345(9)	C(112)-H(11E)	0.9800
O(102)-C(115)	1.464(10)	C(113)-H(11F)	0.9800
O(103)-C(119)	1.270(10)	C(113)-H(11G)	0.9800
O(104)-C(119)	1.223(10)	C(113)-H(11H)	0.9800
O(105)-C(121)	1.264(10)	C(115)-C(116)	1.544(10)
O(106)-C(121)	1.207(10)	C(115)-H(11I)	0.9900
O(107)-H(171)	0.851(9)	C(115)-H(11J)	0.9900
O(107)-H(172)	0.848(9)	C(116)-C(117)	1.519(10)
N(101)-C(109)	1.300(9)	C(116)-C(118)	1.526(10)
N(101)-C(111)	1.492(10)	C(117)-H(11K)	0.9800
N(102)-C(114)	1.304(9)	C(117)-H(11L)	0.9800
N(102)-C(116)	1.487(9)	C(117)-H(11M)	0.9800
C(101)-C(102)	1.394(9)	C(118)-H(11N)	0.9800
C(101)-C(106)	1.400(9)	C(118)-H(11O)	0.9800
C(102)-C(103)	1.407(9)	C(118)-H(11P)	0.9800
C(102)-C(109)	1.460(9)	F(101)-C(120)	1.327(10)
C(103)-C(104)	1.392(10)	F(102)-C(120)	1.343(10)
C(103)-C(107)	1.497(10)	F(103)-C(120)	1.319(10)
C(104)-C(105)	1.403(10)	C(119)-C(120)	1.544(10)
C(104)-H(104)	0.9500	C(121)-C(122)	1.542(7)
C(105)-C(106)	1.407(9)	C(122)-F(105)	1.330(7)
C(105)-C(108)	1.499(10)	C(122)-F(106)	1.333(7)
C(106)-C(114)	1.462(9)	C(122)-F(104)	1.335(7)
C(107)-H(10C)	0.9800	C(222)-F(205)	1.328(7)
C(107)-H(10D)	0.9800	C(222)-F(206)	1.335(7)
C(107)-H(10E)	0.9800	C(222)-F(204)	1.335(7)

C(1)-Ir(1A)-N(2)	79.69(11)	C(4)-C(3)-C(7)	120.5(3)
C(1)-Ir(1A)-O(5)	84.71(9)	C(2)-C(3)-C(7)	122.7(3)
N(2)-Ir(1A)-O(5)	87.61(9)	C(3)-C(4)-C(5)	125.2(3)
C(1)-Ir(1A)-O(3)	88.80(9)	C(3)-C(4)-H(4)	117.4
N(2)-Ir(1A)-O(3)	88.90(9)	C(5)-C(4)-H(4)	117.4
O(5)-Ir(1A)-O(3)	173.09(8)	C(6)-C(5)-C(4)	116.3(3)
C(1)-Ir(1A)-N(1)	79.60(11)	C(6)-C(5)-C(8)	122.7(3)
N(2)-Ir(1A)-N(1)	159.26(10)	C(4)-C(5)-C(8)	121.1(3)
O(5)-Ir(1A)-N(1)	91.53(9)	C(1)-C(6)-C(5)	120.0(3)
O(3)-Ir(1A)-N(1)	89.62(9)	C(1)-C(6)-C(14)	109.2(2)
C(1)-Ir(1A)-O(7)	176.61(10)	C(5)-C(6)-C(14)	130.8(3)
N(2)-Ir(1A)-O(7)	96.93(9)	C(3)-C(7)-H(7A)	109.5
O(5)-Ir(1A)-O(7)	95.05(8)	C(3)-C(7)-H(7B)	109.5
O(3)-Ir(1A)-O(7)	91.29(8)	H(7A)-C(7)-H(7B)	109.5
N(1)-Ir(1A)-O(7)	103.79(9)	C(3)-C(7)-H(7C)	109.5
C(9)-O(1)-C(10)	106.0(2)	H(7A)-C(7)-H(7C)	109.5
C(14)-O(2)-C(15)	105.4(2)	H(7B)-C(7)-H(7C)	109.5
C(19)-O(3)-Ir(1A)	127.01(18)	C(5)-C(8)-H(8A)	109.5
C(21)-O(5)-Ir(1A)	125.98(17)	C(5)-C(8)-H(8B)	109.5
Ir(1A)-O(7)-H(71)	108(3)	H(8A)-C(8)-H(8B)	109.5
Ir(1A)-O(7)-H(72)	124(3)	C(5)-C(8)-H(8C)	109.5
H(71)-O(7)-H(72)	109.2(16)	H(8A)-C(8)-H(8C)	109.5
C(9)-N(1)-C(11)	109.9(2)	H(8B)-C(8)-H(8C)	109.5
C(9)-N(1)-Ir(1A)	112.7(2)	N(1)-C(9)-O(1)	116.1(3)
C(11)-N(1)-Ir(1A)	137.41(19)	N(1)-C(9)-C(2)	119.6(3)
C(14)-N(2)-C(16)	109.5(2)	O(1)-C(9)-C(2)	124.2(3)
C(14)-N(2)-Ir(1A)	113.6(2)	O(1)-C(10)-C(11)	106.0(3)
C(16)-N(2)-Ir(1A)	136.70(18)	O(1)-C(10)-H(10A)	110.5
C(2)-C(1)-C(6)	122.0(3)	C(11)-C(10)-H(10A)	110.5
C(2)-C(1)-Ir(1A)	119.2(2)	O(1)-C(10)-H(10B)	110.5
C(6)-C(1)-Ir(1A)	118.7(2)	C(11)-C(10)-H(10B)	110.5
C(1)-C(2)-C(3)	119.7(3)	H(10A)-C(10)-H(10B)	108.7
C(1)-C(2)-C(9)	108.8(2)	N(1)-C(11)-C(12)	111.0(2)
C(3)-C(2)-C(9)	131.5(3)	N(1)-C(11)-C(13)	109.1(3)
C(4)-C(3)-C(2)	116.8(3)	C(12)-C(11)-C(13)	111.5(3)

N(1)-C(11)-C(10)	100.1(3)	C(16)-C(18)-H(18A)	109.5
C(12)-C(11)-C(10)	112.1(3)	C(16)-C(18)-H(18B)	109.5
C(13)-C(11)-C(10)	112.6(3)	H(18A)-C(18)-H(18B)	109.5
C(11)-C(12)-H(12A)	109.5	C(16)-C(18)-H(18C)	109.5
C(11)-C(12)-H(12B)	109.5	H(18A)-C(18)-H(18C)	109.5
H(12A)-C(12)-H(12B)	109.5	H(18B)-C(18)-H(18C)	109.5
C(11)-C(12)-H(12C)	109.5	O(4)-C(19)-O(3)	130.8(3)
H(12A)-C(12)-H(12C)	109.5	O(4)-C(19)-C(20)	118.5(3)
H(12B)-C(12)-H(12C)	109.5	O(3)-C(19)-C(20)	110.8(2)
C(11)-C(13)-H(13A)	109.5	F(3)-C(20)-F(1)	107.9(3)
C(11)-C(13)-H(13B)	109.5	F(3)-C(20)-F(2)	106.6(3)
H(13A)-C(13)-H(13B)	109.5	F(1)-C(20)-F(2)	106.5(2)
C(11)-C(13)-H(13C)	109.5	F(3)-C(20)-C(19)	112.5(2)
H(13A)-C(13)-H(13C)	109.5	F(1)-C(20)-C(19)	111.9(2)
H(13B)-C(13)-H(13C)	109.5	F(2)-C(20)-C(19)	111.0(2)
N(2)-C(14)-O(2)	116.3(3)	O(6)-C(21)-O(5)	130.1(2)
N(2)-C(14)-C(6)	118.8(3)	O(6)-C(21)-C(22A)	116.8(3)
O(2)-C(14)-C(6)	124.9(3)	O(5)-C(21)-C(22A)	112.2(3)
O(2)-C(15)-C(16)	105.9(2)	F(5A)-C(22A)-F(6A)	106.5(5)
O(2)-C(15)-H(15A)	110.6	F(5A)-C(22A)-F(4A)	106.3(6)
C(16)-C(15)-H(15A)	110.6	F(6A)-C(22A)-F(4A)	107.1(6)
O(2)-C(15)-H(15B)	110.6	F(5A)-C(22A)-C(21)	114.2(5)
C(16)-C(15)-H(15B)	110.6	F(6A)-C(22A)-C(21)	111.0(4)
H(15A)-C(15)-H(15B)	108.7	F(4A)-C(22A)-C(21)	111.4(6)
N(2)-C(16)-C(17)	110.8(3)	F(5B)-C(22B)-F(6B)	107.2(6)
N(2)-C(16)-C(18)	108.7(2)	F(5B)-C(22B)-F(4B)	107.3(6)
C(17)-C(16)-C(18)	111.7(3)	F(6B)-C(22B)-F(4B)	106.3(6)
N(2)-C(16)-C(15)	100.2(2)	C(101)-Ir(1B)-N(101)	80.6(5)
C(17)-C(16)-C(15)	112.2(3)	C(101)-Ir(1B)-O(105)	84.0(7)
C(18)-C(16)-C(15)	112.8(3)	N(101)-Ir(1B)-O(105)	92.7(7)
C(16)-C(17)-H(17A)	109.5	C(101)-Ir(1B)-O(103)	88.9(7)
C(16)-C(17)-H(17B)	109.5	N(101)-Ir(1B)-O(103)	90.1(7)
H(17A)-C(17)-H(17B)	109.5	O(105)-Ir(1B)-O(103)	171.8(7)
C(16)-C(17)-H(17C)	109.5	C(101)-Ir(1B)-N(102)	79.0(5)
H(17A)-C(17)-H(17C)	109.5	N(101)-Ir(1B)-N(102)	159.5(5)
H(17B)-C(17)-H(17C)	109.5	O(105)-Ir(1B)-N(102)	86.8(6)

O(103)-Ir(1B)-N(102)	87.9(7)	C(105)-C(106)-C(114)	130.2(11)
C(101)-Ir(1B)-O(107)	174.9(5)	C(103)-C(107)-H(10C)	109.5
N(101)-Ir(1B)-O(107)	104.5(5)	C(103)-C(107)-H(10D)	109.5
O(105)-Ir(1B)-O(107)	95.6(5)	H(10C)-C(107)-H(10D)	109.5
O(103)-Ir(1B)-O(107)	91.1(5)	C(103)-C(107)-H(10E)	109.5
N(102)-Ir(1B)-O(107)	95.9(5)	H(10C)-C(107)-H(10E)	109.5
C(109)-O(101)-C(110)	106.0(10)	H(10D)-C(107)-H(10E)	109.5
C(114)-O(102)-C(115)	105.7(9)	C(105)-C(108)-H(10F)	109.5
C(119)-O(103)-Ir(1B)	125.9(11)	C(105)-C(108)-H(10G)	109.5
C(121)-O(105)-Ir(1B)	127.9(12)	H(10F)-C(108)-H(10G)	109.5
Ir(1B)-O(107)-H(171)	102.3(7)	C(105)-C(108)-H(10H)	109.5
Ir(1B)-O(107)-H(172)	117.6(9)	H(10F)-C(108)-H(10H)	109.5
H(171)-O(107)-H(172)	110.1(12)	H(10G)-C(108)-H(10H)	109.5
C(109)-N(101)-C(111)	110.9(8)	N(101)-C(109)-O(101)	114.6(10)
C(109)-N(101)-Ir(1B)	112.6(7)	N(101)-C(109)-C(102)	119.2(9)
C(111)-N(101)-Ir(1B)	136.5(8)	O(101)-C(109)-C(102)	126.2(11)
C(114)-N(102)-C(116)	109.3(8)	O(101)-C(110)-C(111)	105.2(10)
C(114)-N(102)-Ir(1B)	113.9(7)	O(101)-C(110)-H(11A)	110.7
C(116)-N(102)-Ir(1B)	136.6(8)	C(111)-C(110)-H(11A)	110.7
C(102)-C(101)-C(106)	123.2(8)	O(101)-C(110)-H(11B)	110.7
C(102)-C(101)-Ir(1B)	117.5(7)	C(111)-C(110)-H(11B)	110.7
C(106)-C(101)-Ir(1B)	119.2(7)	H(11A)-C(110)-H(11B)	108.8
C(101)-C(102)-C(103)	118.8(9)	N(101)-C(111)-C(112)	111.1(13)
C(101)-C(102)-C(109)	110.0(8)	N(101)-C(111)-C(113)	108.3(13)
C(103)-C(102)-C(109)	131.1(10)	C(112)-C(111)-C(113)	112.2(13)
C(104)-C(103)-C(102)	116.3(11)	N(101)-C(111)-C(110)	99.2(8)
C(104)-C(103)-C(107)	122.6(13)	C(112)-C(111)-C(110)	112.0(13)
C(102)-C(103)-C(107)	121.1(13)	C(113)-C(111)-C(110)	113.3(13)
C(103)-C(104)-C(105)	126.8(12)	C(111)-C(112)-H(11C)	109.5
C(103)-C(104)-H(104)	116.6	C(111)-C(112)-H(11D)	109.5
C(105)-C(104)-H(104)	116.6	H(11C)-C(112)-H(11D)	109.5
C(104)-C(105)-C(106)	115.1(11)	C(111)-C(112)-H(11E)	109.5
C(104)-C(105)-C(108)	121.2(13)	H(11C)-C(112)-H(11E)	109.5
C(106)-C(105)-C(108)	123.5(13)	H(11D)-C(112)-H(11E)	109.5
C(101)-C(106)-C(105)	119.6(10)	C(111)-C(113)-H(11F)	109.5
C(101)-C(106)-C(114)	109.8(9)	C(111)-C(113)-H(11G)	109.5

H(11F)-C(113)-H(11G)	109.5	C(116)-C(118)-H(11O)	109.5
C(111)-C(113)-H(11H)	109.5	H(11N)-C(118)-H(11O)	109.5
H(11F)-C(113)-H(11H)	109.5	C(116)-C(118)-H(11P)	109.5
H(11G)-C(113)-H(11H)	109.5	H(11N)-C(118)-H(11P)	109.5
N(102)-C(114)-O(102)	116.9(9)	H(11O)-C(118)-H(11P)	109.5
N(102)-C(114)-C(106)	117.9(9)	O(104)-C(119)-O(103)	131(2)
O(102)-C(114)-C(106)	125.0(11)	O(104)-C(119)-C(120)	118.5(16)
O(102)-C(115)-C(116)	106.7(9)	O(103)-C(119)-C(120)	108.9(12)
O(102)-C(115)-H(11I)	110.4	F(103)-C(120)-F(101)	109.3(14)
C(116)-C(115)-H(11I)	110.4	F(103)-C(120)-F(102)	105.7(14)
O(102)-C(115)-H(11J)	110.4	F(101)-C(120)-F(102)	108.0(13)
C(116)-C(115)-H(11J)	110.4	F(103)-C(120)-C(119)	111.8(13)
H(11I)-C(115)-H(11J)	108.6	F(101)-C(120)-C(119)	111.4(13)
N(102)-C(116)-C(117)	112.5(13)	F(102)-C(120)-C(119)	110.5(14)
N(102)-C(116)-C(118)	109.0(13)	O(106)-C(121)-O(105)	126.1(19)
C(117)-C(116)-C(118)	110.8(12)	O(106)-C(121)-C(122)	113.5(16)
N(102)-C(116)-C(115)	101.3(8)	O(105)-C(121)-C(122)	110.7(14)
C(117)-C(116)-C(115)	111.4(13)	F(105)-C(122)-F(106)	107.0(8)
C(118)-C(116)-C(115)	111.5(13)	F(105)-C(122)-F(104)	106.9(8)
C(116)-C(117)-H(11K)	109.5	F(106)-C(122)-F(104)	107.0(8)
C(116)-C(117)-H(11L)	109.5	F(105)-C(122)-C(121)	112.5(8)
H(11K)-C(117)-H(11L)	109.5	F(106)-C(122)-C(121)	111.5(8)
C(116)-C(117)-H(11M)	109.5	F(104)-C(122)-C(121)	111.6(8)
H(11K)-C(117)-H(11M)	109.5	F(205)-C(222)-F(206)	107.0(8)
H(11L)-C(117)-H(11M)	109.5	F(205)-C(222)-F(204)	106.9(8)
C(116)-C(118)-H(11N)	109.5	F(206)-C(222)-F(204)	106.6(8)

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for IrNONO_COOCF3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1A)	22(1)	15(1)	14(1)	1(1)	5(1)	0(1)
O(1)	46(1)	26(1)	25(1)	8(1)	0(1)	7(1)
O(2)	30(1)	36(1)	31(1)	8(1)	17(1)	10(1)
O(3)	25(1)	19(1)	22(1)	2(1)	9(1)	1(1)
O(4)	32(1)	28(2)	31(1)	0(1)	17(1)	0(1)
O(5)	32(1)	22(1)	19(1)	-1(1)	8(1)	-6(1)
O(6)	42(1)	41(2)	37(1)	-14(1)	22(1)	-12(1)
O(7)	30(1)	29(1)	19(1)	1(1)	9(1)	2(1)
N(1)	30(1)	18(1)	20(1)	2(1)	2(1)	3(1)
N(2)	22(1)	23(1)	20(1)	6(1)	8(1)	2(1)
C(1)	28(1)	16(1)	16(1)	1(1)	5(1)	-5(1)
C(2)	34(1)	17(1)	18(1)	4(1)	3(1)	-4(1)
C(3)	40(2)	25(1)	20(1)	3(1)	6(1)	-11(1)
C(4)	42(2)	30(2)	18(1)	1(1)	10(1)	-11(1)
C(5)	37(2)	22(1)	22(1)	-4(1)	15(1)	-8(1)
C(6)	27(1)	21(1)	19(1)	2(1)	10(1)	-3(1)
C(7)	52(2)	41(2)	19(1)	11(1)	5(1)	-8(2)
C(8)	37(2)	36(2)	29(2)	-6(1)	19(1)	-4(1)
C(9)	31(1)	15(1)	23(1)	3(1)	-1(1)	-2(1)
C(10)	41(2)	32(2)	34(2)	5(1)	0(1)	14(1)
C(11)	34(2)	20(1)	28(2)	4(1)	4(1)	10(1)
C(12)	33(2)	39(2)	46(2)	12(2)	11(2)	14(1)
C(13)	47(2)	26(2)	34(2)	-2(1)	4(1)	11(1)
C(14)	24(1)	21(1)	25(1)	2(1)	10(1)	0(1)
C(15)	31(2)	56(2)	39(2)	22(2)	19(1)	18(2)
C(16)	21(1)	34(2)	25(1)	12(1)	7(1)	8(1)
C(17)	28(2)	50(2)	28(2)	9(1)	2(1)	5(1)
C(18)	31(1)	32(2)	37(2)	18(1)	14(1)	8(1)
F(1)	38(1)	33(1)	43(1)	6(1)	20(1)	-9(1)
F(2)	38(1)	19(1)	66(2)	1(1)	25(1)	4(1)
F(3)	39(1)	35(1)	34(1)	4(1)	-1(1)	-4(1)

C(19)	20(1)	19(1)	26(1)	4(1)	6(1)	3(1)
C(20)	25(1)	22(1)	32(2)	5(1)	13(1)	1(1)
C(21)	24(1)	20(1)	22(1)	1(1)	5(1)	1(1)
C(22A)	31(3)	18(3)	26(3)	-1(2)	8(3)	-2(2)
F(4A)	38(3)	24(3)	66(5)	-19(3)	16(3)	-10(2)
F(5A)	53(3)	52(3)	36(3)	10(2)	14(3)	-20(2)
F(6A)	25(2)	40(2)	64(3)	10(2)	-1(2)	1(2)
C(22B)	38(4)	23(3)	28(3)	-4(3)	13(3)	-5(3)
F(4B)	37(3)	53(4)	27(2)	-15(3)	13(2)	-17(3)
F(5B)	42(3)	51(4)	74(5)	-23(3)	38(3)	-14(3)
F(6B)	81(5)	33(2)	55(4)	18(2)	2(3)	-7(3)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for IrNONO_COOCF3.

	x	y	z	U(eq)
H(71)	3330(30)	2130(30)	4150(30)	40
H(72)	4260(40)	3400(20)	4590(30)	40
H(4)	5713	2115	-890	39
H(7A)	2470	3074	-1288	61
H(7B)	4087	3525	-1494	61
H(7C)	3609	4481	-718	61
H(8A)	8558	1270	587	52
H(8B)	7324	571	-478	52
H(8C)	7351	-98	471	52
H(10A)	-84	3995	853	45
H(10B)	886	5517	1170	45
H(12A)	1202	3385	3266	58
H(12B)	242	2604	2159	58
H(12C)	-212	3929	2593	58
H(13A)	3334	6161	2642	57
H(13B)	3336	5398	3546	57
H(13C)	1925	6106	3093	57
H(15A)	9226	819	3786	46
H(15B)	8223	-692	3468	46
H(17A)	6752	1958	4969	56
H(17B)	8343	2400	4729	56
H(17C)	8135	1172	5288	56
H(18A)	4799	-156	3941	47
H(18B)	6146	-949	4346	47
H(18C)	5308	-1104	3177	47
H(171)	3189	2100	4034	65
H(172)	4109	3363	4494	65
H(104)	4882	2877	-1093	52
H(10C)	1950	4557	-663	65
H(10D)	2029	3560	-1587	65

H(10E)	3362	4889	-1097	65
H(10F)	6781	1609	-864	65
H(10G)	6653	505	-188	65
H(10H)	7876	1903	272	65
H(11A)	-652	4059	1101	52
H(11B)	140	5622	1488	52
H(11C)	-221	2663	2282	65
H(11D)	-393	3894	3009	65
H(11E)	1037	3169	3368	65
H(11F)	2887	6239	2864	65
H(11G)	2959	5400	3734	65
H(11H)	1536	6129	3366	65
H(11I)	8837	614	3188	52
H(11J)	7472	-711	2734	52
H(11K)	8456	2523	4171	65
H(11L)	8360	1360	4802	65
H(11M)	7087	2273	4652	65
H(11N)	4968	-843	3028	65
H(11O)	4950	178	3959	65
H(11P)	6243	-715	4094	65

Table S8. Torsion angles [°] for IrNONO_COOCF3.

C(6)-C(1)-C(2)-C(3)	-0.4(4)	Ir(1A)-N(1)-C(11)-C(13)	69.5(4)
Ir(1A)-C(1)-C(2)-C(3)	176.9(2)	C(9)-N(1)-C(11)-C(10)	10.1(3)
C(6)-C(1)-C(2)-C(9)	179.9(2)	Ir(1A)-N(1)-C(11)-C(10)	-172.1(2)
Ir(1A)-C(1)-C(2)-C(9)	-2.7(3)	O(1)-C(10)-C(11)-N(1)	-13.6(3)
C(1)-C(2)-C(3)-C(4)	1.0(4)	O(1)-C(10)-C(11)-C(12)	-131.3(3)
C(9)-C(2)-C(3)-C(4)	-179.4(3)	O(1)-C(10)-C(11)-C(13)	102.0(3)
C(1)-C(2)-C(3)-C(7)	-179.1(3)	C(16)-N(2)-C(14)-O(2)	-4.2(3)
C(9)-C(2)-C(3)-C(7)	0.5(5)	Ir(1A)-N(2)-C(14)-O(2)	-179.74(19)
C(2)-C(3)-C(4)-C(5)	-0.4(5)	C(16)-N(2)-C(14)-C(6)	176.0(2)
C(7)-C(3)-C(4)-C(5)	179.8(3)	Ir(1A)-N(2)-C(14)-C(6)	0.4(3)
C(3)-C(4)-C(5)-C(6)	-0.9(4)	C(15)-O(2)-C(14)-N(2)	-7.0(3)
C(3)-C(4)-C(5)-C(8)	178.8(3)	C(15)-O(2)-C(14)-C(6)	172.9(3)
C(2)-C(1)-C(6)-C(5)	-1.0(4)	C(1)-C(6)-C(14)-N(2)	-1.5(4)
Ir(1A)-C(1)-C(6)-C(5)	-178.3(2)	C(5)-C(6)-C(14)-N(2)	178.9(3)
C(2)-C(1)-C(6)-C(14)	179.4(2)	C(1)-C(6)-C(14)-O(2)	178.6(3)
Ir(1A)-C(1)-C(6)-C(14)	2.1(3)	C(5)-C(6)-C(14)-O(2)	-1.0(5)
C(4)-C(5)-C(6)-C(1)	1.5(4)	C(14)-O(2)-C(15)-C(16)	14.5(3)
C(8)-C(5)-C(6)-C(1)	-178.1(3)	C(14)-N(2)-C(16)-C(17)	131.1(3)
C(4)-C(5)-C(6)-C(14)	-178.9(3)	Ir(1A)-N(2)-C(16)-C(17)	-54.8(3)
C(8)-C(5)-C(6)-C(14)	1.4(5)	C(14)-N(2)-C(16)-C(18)	-105.9(3)
C(11)-N(1)-C(9)-O(1)	-2.6(3)	Ir(1A)-N(2)-C(16)-C(18)	68.2(4)
Ir(1A)-N(1)-C(9)-O(1)	179.05(19)	C(14)-N(2)-C(16)-C(15)	12.5(3)
C(11)-N(1)-C(9)-C(2)	178.0(2)	Ir(1A)-N(2)-C(16)-C(15)	-173.4(2)
Ir(1A)-N(1)-C(9)-C(2)	-0.3(3)	O(2)-C(15)-C(16)-N(2)	-16.0(3)
C(10)-O(1)-C(9)-N(1)	-7.0(3)	O(2)-C(15)-C(16)-C(17)	-133.5(3)
C(10)-O(1)-C(9)-C(2)	172.4(3)	O(2)-C(15)-C(16)-C(18)	99.4(3)
C(1)-C(2)-C(9)-N(1)	1.9(4)	Ir(1A)-O(3)-C(19)-O(4)	5.5(8)
C(3)-C(2)-C(9)-N(1)	-177.8(3)	Ir(1A)-O(3)-C(19)-C(20)	-173.19(18)
C(1)-C(2)-C(9)-O(1)	-177.4(3)	O(4)-C(19)-C(20)-F(3)	116.3(6)
C(3)-C(2)-C(9)-O(1)	2.9(5)	O(3)-C(19)-C(20)-F(3)	-64.8(4)
C(9)-O(1)-C(10)-C(11)	13.0(3)	O(4)-C(19)-C(20)-F(1)	-5.4(6)
C(9)-N(1)-C(11)-C(12)	128.6(3)	O(3)-C(19)-C(20)-F(1)	173.5(3)
Ir(1A)-N(1)-C(11)-C(12)	-53.7(4)	O(4)-C(19)-C(20)-F(2)	-124.3(6)
C(9)-N(1)-C(11)-C(13)	-108.2(3)	O(3)-C(19)-C(20)-F(2)	54.6(4)

Ir(1A)-O(5)-C(21)-O(6)	1.6(5)	C(101)-C(102)-C(109)-O(101)	-180(4)
Ir(1A)-O(5)-C(21)-C(22A)	170.0(3)	C(103)-C(102)-C(109)-O(101)	2(8)
O(6)-C(21)-C(22A)-F(5A)	-156.3(5)	C(109)-O(101)-C(110)-C(111)	20(4)
O(5)-C(21)-C(22A)-F(5A)	33.6(6)	C(109)-N(101)-C(111)-C(112)	128(3)
O(6)-C(21)-C(22A)-F(6A)	83.3(6)	Ir(1B)-N(101)-C(111)-C(112)	-51(3)
O(5)-C(21)-C(22A)-F(6A)	-86.8(5)	C(109)-N(101)-C(111)-C(113)	-108(3)
O(6)-C(21)-C(22A)-F(4A)	-35.9(7)	Ir(1B)-N(101)-C(111)-C(113)	73(3)
O(5)-C(21)-C(22A)-F(4A)	154.0(6)	C(109)-N(101)-C(111)-C(110)	10(3)
C(106)-C(101)-C(102)-C(103)	-2(6)	Ir(1B)-N(101)-C(111)-C(110)	-169(2)
Ir(1B)-C(101)-C(102)-C(103)	174(3)	O(101)-C(110)-C(111)-N(101)	-18(3)
C(106)-C(101)-C(102)-C(109)	180(4)	O(101)-C(110)-C(111)-C(112)	-135(3)
Ir(1B)-C(101)-C(102)-C(109)	-4(4)	O(101)-C(110)-C(111)-C(113)	97(3)
C(101)-C(102)-C(103)-C(104)	0(6)	C(116)-N(102)-C(114)-O(102)	3(5)
C(109)-C(102)-C(103)-C(104)	178(5)	Ir(1B)-N(102)-C(114)-O(102)	179(3)
C(101)-C(102)-C(103)-C(107)	-180(4)	C(116)-N(102)-C(114)-C(106)	178(3)
C(109)-C(102)-C(103)-C(107)	-2(8)	Ir(1B)-N(102)-C(114)-C(106)	-6(5)
C(102)-C(103)-C(104)-C(105)	2(8)	C(115)-O(102)-C(114)-N(102)	-2(5)
C(107)-C(103)-C(104)-C(105)	-178(5)	C(115)-O(102)-C(114)-C(106)	-176(4)
C(103)-C(104)-C(105)-C(106)	-2(8)	C(101)-C(106)-C(114)-N(102)	4(6)
C(103)-C(104)-C(105)-C(108)	-177(5)	C(105)-C(106)-C(114)-N(102)	177(4)
C(102)-C(101)-C(106)-C(105)	2(6)	C(101)-C(106)-C(114)-O(102)	178(4)
Ir(1B)-C(101)-C(106)-C(105)	-174(3)	C(105)-C(106)-C(114)-O(102)	-9(8)
C(102)-C(101)-C(106)-C(114)	176(4)	C(114)-O(102)-C(115)-C(116)	-1(4)
Ir(1B)-C(101)-C(106)-C(114)	0(4)	C(114)-N(102)-C(116)-C(117)	116(3)
C(104)-C(105)-C(106)-C(101)	0(6)	Ir(1B)-N(102)-C(116)-C(117)	-59(3)
C(108)-C(105)-C(106)-C(101)	175(4)	C(114)-N(102)-C(116)-C(118)	-121(3)
C(104)-C(105)-C(106)-C(114)	-173(5)	Ir(1B)-N(102)-C(116)-C(118)	64(3)
C(108)-C(105)-C(106)-C(114)	3(8)	C(114)-N(102)-C(116)-C(115)	-3(3)
C(111)-N(101)-C(109)-O(101)	2(5)	Ir(1B)-N(102)-C(116)-C(115)	-178(2)
Ir(1B)-N(101)-C(109)-O(101)	-178(3)	O(102)-C(115)-C(116)-N(102)	2(3)
C(111)-N(101)-C(109)-C(102)	180(3)	O(102)-C(115)-C(116)-C(117)	-118(3)
Ir(1B)-N(101)-C(109)-C(102)	-1(5)	O(102)-C(115)-C(116)-C(118)	118(3)
C(110)-O(101)-C(109)-N(101)	-15(5)	Ir(1B)-O(103)-C(119)-O(104)	19(10)
C(110)-O(101)-C(109)-C(102)	168(4)	Ir(1B)-O(103)-C(119)-C(120)	-177.7(16)
C(101)-C(102)-C(109)-N(101)	3(6)	O(104)-C(119)-C(120)-F(103)	131(8)
C(103)-C(102)-C(109)-N(101)	-175(5)	O(103)-C(119)-C(120)-F(103)	-35(4)

O(104)-C(119)-C(120)-F(101)	8(8)	O(106)-C(121)-C(122)-F(105)	157(4)
O(103)-C(119)-C(120)-F(101)	-157(4)	O(105)-C(121)-C(122)-F(105)	-55(4)
O(104)-C(119)-C(120)-F(102)	-112(8)	O(106)-C(121)-C(122)-F(106)	-83(4)
O(103)-C(119)-C(120)-F(102)	83(4)	O(105)-C(121)-C(122)-F(106)	66(4)
Ir(1B)-O(105)-C(121)-O(106)	-29(5)	O(106)-C(121)-C(122)-F(104)	37(4)
Ir(1B)-O(105)-C(121)-C(122)	-173(2)	O(105)-C(121)-C(122)-F(104)	-175(4)

Table S9. Hydrogen bonds for IrNONO_COOCF3 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(7)-H(71)...O(4)	0.855(10)	1.864(18)	2.636(4)	149(3)
O(7)-H(72)...O(6)#1	0.852(10)	2.006(15)	2.835(3)	164(3)
O(7)-H(72)...O(6)	0.852(10)	2.27(3)	2.739(3)	115(3)
O(107)-H(171)...O(104)	0.851(9)	1.83(4)	2.61(4)	150(3)
O(107)-H(172)...O(106)#1	0.848(9)	1.90(2)	2.71(3)	159.6(12)
O(107)-H(172)...O(106)	0.848(9)	2.46(3)	2.97(3)	119.2(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

2. (Phebox)Ir(mesityl)(OAc) **(3)**

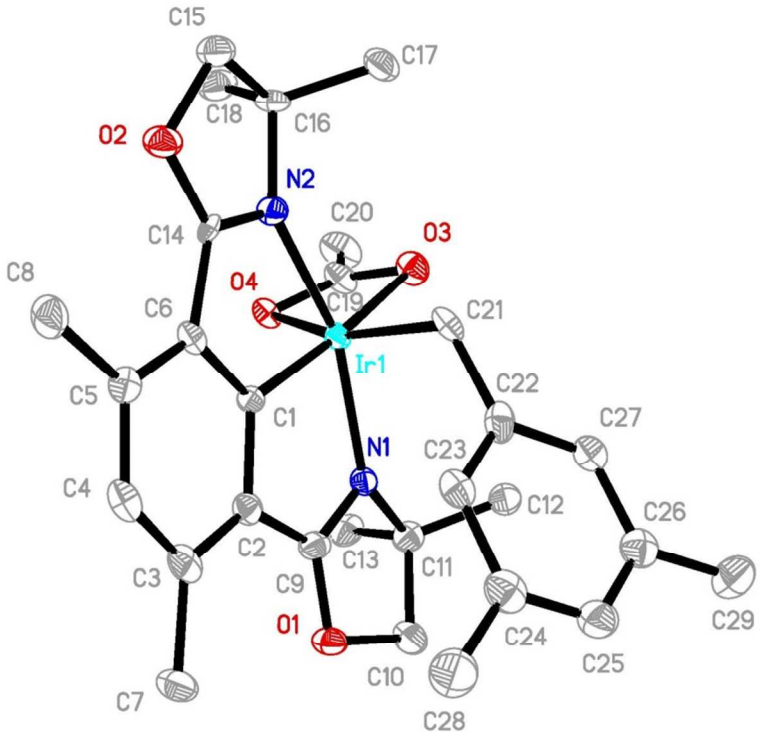


Table S10. Crystal data and structure refinement for iroac3m_Pbca.

Identification code	iroac3m_Pbca	
Empirical formula	C29 H37 Ir N2 O4	
Formula weight	669.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 20.532(3) Å	α= 90°.
	b = 11.9277(18) Å	β= 90°.
	c = 22.489(3) Å	γ = 90°.
Volume	5507.5(14) $Å^3$	
Z	8	
Density (calculated)	1.616 Mg/m^3	
Absorption coefficient	4.884 mm^{-1}	
F(000)	2672	

Crystal size	0.360 x 0.200 x 0.045 mm^3
Theta range for data collection	1.811 to 26.362°.
Index ranges	-22<=h<=25, -14<=k<=14, -28<=l<=28
Reflections collected	30856
Independent reflections	5631 [R(int) = 0.0920]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4524
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5631 / 0 / 334
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1039
R indices (all data)	R1 = 0.0617, wR2 = 0.1153
Extinction coefficient	n/a
Largest diff. peak and hole	2.864 and -1.983 $e.Å^{-3}$

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for iroac3m_Pbca. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	6484(1)	8732(1)	2654(1)	14(1)
N(1)	5844(2)	9776(4)	3091(2)	15(1)
N(2)	7351(3)	8023(4)	2418(2)	17(1)
O(1)	5726(2)	11075(3)	3808(2)	20(1)
O(2)	8413(2)	7841(4)	2648(2)	22(1)
O(3)	5839(2)	8077(4)	1902(2)	22(1)
O(4)	6380(2)	9652(3)	1779(2)	18(1)
C(1)	7058(3)	9447(4)	3209(3)	14(1)
C(2)	6812(3)	10240(5)	3619(3)	17(1)
C(3)	7220(3)	10705(5)	4057(3)	21(1)
C(4)	7868(3)	10334(5)	4070(3)	21(1)
C(5)	8134(3)	9565(5)	3667(3)	17(1)
C(6)	7712(3)	9123(5)	3234(3)	17(1)
C(7)	6984(3)	11564(5)	4504(3)	24(1)
C(8)	8845(3)	9248(5)	3717(3)	25(1)
C(9)	6122(3)	10381(5)	3509(3)	19(1)
C(10)	5072(3)	10769(5)	3624(3)	24(1)
C(11)	5164(3)	10199(5)	3023(3)	20(1)
C(12)	4686(3)	9238(5)	2919(3)	23(1)
C(13)	5137(3)	11026(5)	2512(3)	23(1)
C(14)	7833(3)	8321(5)	2760(3)	14(1)
C(15)	8285(3)	6973(5)	2199(3)	22(1)
C(16)	7598(3)	7246(5)	1953(3)	18(1)
C(17)	7169(3)	6192(5)	1940(3)	24(1)
C(18)	7617(3)	7829(5)	1353(3)	26(2)
C(19)	5983(3)	8909(5)	1578(3)	20(1)
C(20)	5700(4)	9043(6)	970(3)	31(2)
C(21)	6421(3)	7434(5)	3287(3)	18(1)
C(22)	6063(3)	7663(5)	3844(3)	22(1)
C(23)	6374(3)	8158(5)	4333(3)	20(1)
C(24)	6024(3)	8434(5)	4848(3)	27(2)

C(25)	5366(3)	8182(5)	4877(3)	28(2)
C(26)	5054(3)	7644(5)	4410(3)	25(1)
C(27)	5412(3)	7389(5)	3905(3)	22(1)
C(28)	6373(4)	8997(7)	5360(3)	36(2)
C(29)	4334(3)	7345(6)	4451(3)	34(2)

Table S12. Bond lengths [Å] and angles [°] for iroac3m_Pbca.

Ir(1)-C(1)	1.918(6)	C(10)-H(10A)	0.9900
Ir(1)-N(2)	2.042(5)	C(10)-H(10B)	0.9900
Ir(1)-N(1)	2.061(5)	C(11)-C(13)	1.514(8)
Ir(1)-C(21)	2.107(6)	C(11)-C(12)	1.526(8)
Ir(1)-O(4)	2.262(4)	C(12)-H(12A)	0.9800
Ir(1)-O(3)	2.284(4)	C(12)-H(12B)	0.9800
N(1)-C(9)	1.314(8)	C(12)-H(12C)	0.9800
N(1)-C(11)	1.493(7)	C(13)-H(13A)	0.9800
N(2)-C(14)	1.301(7)	C(13)-H(13B)	0.9800
N(2)-C(16)	1.487(7)	C(13)-H(13C)	0.9800
O(1)-C(9)	1.342(7)	C(15)-C(16)	1.549(8)
O(1)-C(10)	1.452(7)	C(15)-H(15A)	0.9900
O(2)-C(14)	1.345(7)	C(15)-H(15B)	0.9900
O(2)-C(15)	1.471(7)	C(16)-C(18)	1.518(8)
O(3)-C(19)	1.265(7)	C(16)-C(17)	1.535(8)
O(4)-C(19)	1.286(7)	C(17)-H(17A)	0.9800
C(1)-C(6)	1.399(8)	C(17)-H(17B)	0.9800
C(1)-C(2)	1.415(8)	C(17)-H(17C)	0.9800
C(2)-C(3)	1.406(8)	C(18)-H(18A)	0.9800
C(2)-C(9)	1.449(9)	C(18)-H(18B)	0.9800
C(3)-C(4)	1.401(9)	C(18)-H(18C)	0.9800
C(3)-C(7)	1.514(8)	C(19)-C(20)	1.495(8)
C(4)-C(5)	1.401(8)	C(20)-H(20A)	0.9800
C(4)-H(4)	0.9500	C(20)-H(20B)	0.9800
C(5)-C(6)	1.405(8)	C(20)-H(20C)	0.9800
C(5)-C(8)	1.514(8)	C(21)-C(22)	1.479(9)
C(6)-C(14)	1.453(8)	C(21)-H(21A)	0.9900
C(7)-H(7A)	0.9800	C(21)-H(21B)	0.9900
C(7)-H(7B)	0.9800	C(22)-C(27)	1.382(9)
C(7)-H(7C)	0.9800	C(22)-C(23)	1.403(9)
C(8)-H(8A)	0.9800	C(23)-C(24)	1.403(9)
C(8)-H(8B)	0.9800	C(23)-H(23)	0.9500
C(8)-H(8C)	0.9800	C(24)-C(25)	1.386(9)
C(10)-C(11)	1.525(9)	C(24)-C(28)	1.513(10)

C(25)-C(26)	1.387(9)	C(28)-H(28B)	0.9800
C(25)-H(25)	0.9500	C(28)-H(28C)	0.9800
C(26)-C(27)	1.386(9)	C(29)-H(29A)	0.9800
C(26)-C(29)	1.523(9)	C(29)-H(29B)	0.9800
C(27)-H(27)	0.9500	C(29)-H(29C)	0.9800
C(28)-H(28A)	0.9800		

C(1)-Ir(1)-N(2)	79.4(2)	C(3)-C(2)-C(9)	131.1(5)
C(1)-Ir(1)-N(1)	79.2(2)	C(1)-C(2)-C(9)	108.3(5)
N(2)-Ir(1)-N(1)	158.50(19)	C(4)-C(3)-C(2)	117.1(6)
C(1)-Ir(1)-C(21)	85.6(2)	C(4)-C(3)-C(7)	120.2(6)
N(2)-Ir(1)-C(21)	85.7(2)	C(2)-C(3)-C(7)	122.7(5)
N(1)-Ir(1)-C(21)	94.7(2)	C(5)-C(4)-C(3)	124.3(6)
C(1)-Ir(1)-O(4)	114.08(19)	C(5)-C(4)-H(4)	117.9
N(2)-Ir(1)-O(4)	93.30(17)	C(3)-C(4)-H(4)	117.9
N(1)-Ir(1)-O(4)	93.55(17)	C(4)-C(5)-C(6)	117.0(5)
C(21)-Ir(1)-O(4)	159.75(19)	C(4)-C(5)-C(8)	119.5(5)
C(1)-Ir(1)-O(3)	171.93(19)	C(6)-C(5)-C(8)	123.5(5)
N(2)-Ir(1)-O(3)	99.91(17)	C(1)-C(6)-C(5)	121.0(5)
N(1)-Ir(1)-O(3)	101.00(17)	C(1)-C(6)-C(14)	108.4(5)
C(21)-Ir(1)-O(3)	102.35(19)	C(5)-C(6)-C(14)	130.6(5)
O(4)-Ir(1)-O(3)	57.86(15)	C(3)-C(7)-H(7A)	109.5
C(9)-N(1)-C(11)	107.1(5)	C(3)-C(7)-H(7B)	109.5
C(9)-N(1)-Ir(1)	113.4(4)	H(7A)-C(7)-H(7B)	109.5
C(11)-N(1)-Ir(1)	138.7(4)	C(3)-C(7)-H(7C)	109.5
C(14)-N(2)-C(16)	109.1(5)	H(7A)-C(7)-H(7C)	109.5
C(14)-N(2)-Ir(1)	113.3(4)	H(7B)-C(7)-H(7C)	109.5
C(16)-N(2)-Ir(1)	137.6(4)	C(5)-C(8)-H(8A)	109.5
C(9)-O(1)-C(10)	105.1(4)	C(5)-C(8)-H(8B)	109.5
C(14)-O(2)-C(15)	105.6(4)	H(8A)-C(8)-H(8B)	109.5
C(19)-O(3)-Ir(1)	91.3(3)	C(5)-C(8)-H(8C)	109.5
C(19)-O(4)-Ir(1)	91.8(3)	H(8A)-C(8)-H(8C)	109.5
C(6)-C(1)-C(2)	120.1(5)	H(8B)-C(8)-H(8C)	109.5
C(6)-C(1)-Ir(1)	119.6(4)	N(1)-C(9)-O(1)	115.8(5)
C(2)-C(1)-Ir(1)	120.2(4)	N(1)-C(9)-C(2)	118.9(5)
C(3)-C(2)-C(1)	120.5(5)	O(1)-C(9)-C(2)	125.3(5)

O(1)-C(10)-C(11)	104.6(5)	N(2)-C(16)-C(15)	100.9(5)
O(1)-C(10)-H(10A)	110.8	C(18)-C(16)-C(15)	113.0(5)
C(11)-C(10)-H(10A)	110.8	C(17)-C(16)-C(15)	111.0(5)
O(1)-C(10)-H(10B)	110.8	C(16)-C(17)-H(17A)	109.5
C(11)-C(10)-H(10B)	110.8	C(16)-C(17)-H(17B)	109.5
H(10A)-C(10)-H(10B)	108.9	H(17A)-C(17)-H(17B)	109.5
N(1)-C(11)-C(13)	109.5(5)	C(16)-C(17)-H(17C)	109.5
N(1)-C(11)-C(10)	100.1(5)	H(17A)-C(17)-H(17C)	109.5
C(13)-C(11)-C(10)	112.1(5)	H(17B)-C(17)-H(17C)	109.5
N(1)-C(11)-C(12)	111.3(5)	C(16)-C(18)-H(18A)	109.5
C(13)-C(11)-C(12)	110.5(5)	C(16)-C(18)-H(18B)	109.5
C(10)-C(11)-C(12)	112.9(5)	H(18A)-C(18)-H(18B)	109.5
C(11)-C(12)-H(12A)	109.5	C(16)-C(18)-H(18C)	109.5
C(11)-C(12)-H(12B)	109.5	H(18A)-C(18)-H(18C)	109.5
H(12A)-C(12)-H(12B)	109.5	H(18B)-C(18)-H(18C)	109.5
C(11)-C(12)-H(12C)	109.5	O(3)-C(19)-O(4)	119.1(5)
H(12A)-C(12)-H(12C)	109.5	O(3)-C(19)-C(20)	121.3(5)
H(12B)-C(12)-H(12C)	109.5	O(4)-C(19)-C(20)	119.6(5)
C(11)-C(13)-H(13A)	109.5	C(19)-C(20)-H(20A)	109.5
C(11)-C(13)-H(13B)	109.5	C(19)-C(20)-H(20B)	109.5
H(13A)-C(13)-H(13B)	109.5	H(20A)-C(20)-H(20B)	109.5
C(11)-C(13)-H(13C)	109.5	C(19)-C(20)-H(20C)	109.5
H(13A)-C(13)-H(13C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(13B)-C(13)-H(13C)	109.5	H(20B)-C(20)-H(20C)	109.5
N(2)-C(14)-O(2)	116.5(5)	C(22)-C(21)-Ir(1)	117.9(4)
N(2)-C(14)-C(6)	118.9(5)	C(22)-C(21)-H(21A)	107.8
O(2)-C(14)-C(6)	124.6(5)	Ir(1)-C(21)-H(21A)	107.8
O(2)-C(15)-C(16)	105.1(5)	C(22)-C(21)-H(21B)	107.8
O(2)-C(15)-H(15A)	110.7	Ir(1)-C(21)-H(21B)	107.8
C(16)-C(15)-H(15A)	110.7	H(21A)-C(21)-H(21B)	107.2
O(2)-C(15)-H(15B)	110.7	C(27)-C(22)-C(23)	117.6(6)
C(16)-C(15)-H(15B)	110.7	C(27)-C(22)-C(21)	121.4(6)
H(15A)-C(15)-H(15B)	108.8	C(23)-C(22)-C(21)	121.0(5)
N(2)-C(16)-C(18)	110.3(5)	C(22)-C(23)-C(24)	120.8(6)
N(2)-C(16)-C(17)	109.2(5)	C(22)-C(23)-H(23)	119.6
C(18)-C(16)-C(17)	111.9(5)	C(24)-C(23)-H(23)	119.6

C(25)-C(24)-C(23)	119.2(6)	C(24)-C(28)-H(28A)	109.5
C(25)-C(24)-C(28)	121.5(6)	C(24)-C(28)-H(28B)	109.5
C(23)-C(24)-C(28)	119.3(6)	H(28A)-C(28)-H(28B)	109.5
C(24)-C(25)-C(26)	121.0(6)	C(24)-C(28)-H(28C)	109.5
C(24)-C(25)-H(25)	119.5	H(28A)-C(28)-H(28C)	109.5
C(26)-C(25)-H(25)	119.5	H(28B)-C(28)-H(28C)	109.5
C(27)-C(26)-C(25)	118.5(6)	C(26)-C(29)-H(29A)	109.5
C(27)-C(26)-C(29)	120.8(6)	C(26)-C(29)-H(29B)	109.5
C(25)-C(26)-C(29)	120.7(6)	H(29A)-C(29)-H(29B)	109.5
C(22)-C(27)-C(26)	122.8(6)	C(26)-C(29)-H(29C)	109.5
C(22)-C(27)-H(27)	118.6	H(29A)-C(29)-H(29C)	109.5
C(26)-C(27)-H(27)	118.6	H(29B)-C(29)-H(29C)	109.5

Table S13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for iroac3m_Pbca. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	13(1)	12(1)	17(1)	-1(1)	0(1)	0(1)
N(1)	12(2)	12(2)	22(3)	0(2)	0(2)	1(2)
N(2)	18(3)	15(2)	20(3)	0(2)	2(2)	2(2)
O(1)	19(2)	19(2)	21(2)	-5(2)	-1(2)	4(2)
O(2)	20(2)	18(2)	27(3)	-3(2)	-1(2)	5(2)
O(3)	20(2)	23(2)	25(2)	-2(2)	-5(2)	-1(2)
O(4)	22(2)	14(2)	19(2)	-1(2)	-2(2)	-2(2)
C(1)	14(3)	8(3)	19(3)	3(2)	3(2)	4(2)
C(2)	19(3)	14(3)	20(3)	1(2)	1(3)	0(2)
C(3)	29(4)	10(3)	24(3)	6(2)	-1(3)	-1(3)
C(4)	24(3)	16(3)	22(3)	2(2)	-6(3)	-4(3)
C(5)	16(3)	16(3)	19(3)	5(2)	-2(2)	1(2)
C(6)	20(3)	12(3)	20(3)	-1(2)	-1(3)	-3(2)
C(7)	26(4)	22(3)	25(3)	-9(3)	-2(3)	1(3)
C(8)	17(3)	23(3)	35(4)	-3(3)	-4(3)	-1(3)
C(9)	23(3)	14(3)	19(3)	2(2)	6(3)	3(3)
C(10)	18(3)	20(3)	33(4)	-4(3)	-3(3)	1(3)
C(11)	21(3)	17(3)	21(3)	3(3)	1(3)	5(2)
C(12)	18(3)	20(3)	31(4)	0(3)	2(3)	4(3)
C(13)	19(3)	21(3)	29(3)	5(3)	4(3)	8(3)
C(14)	6(3)	17(3)	19(3)	-2(2)	4(2)	-1(2)
C(15)	19(3)	22(3)	24(3)	-6(3)	0(3)	3(3)
C(16)	19(3)	15(3)	19(3)	-5(2)	1(3)	6(2)
C(17)	24(3)	15(3)	34(4)	-2(3)	-1(3)	1(3)
C(18)	28(3)	23(3)	29(4)	2(3)	7(3)	7(3)
C(19)	26(3)	17(3)	17(3)	-1(2)	-8(3)	-1(3)
C(20)	42(4)	28(4)	24(3)	-1(3)	-10(3)	4(3)
C(21)	22(3)	10(3)	21(3)	0(2)	-6(3)	-2(2)
C(22)	21(3)	18(3)	27(3)	7(3)	0(3)	-3(3)
C(23)	20(3)	16(3)	24(3)	1(3)	-5(3)	0(3)
C(24)	34(4)	21(3)	25(3)	3(3)	-4(3)	1(3)

C(25)	35(4)	22(3)	27(3)	0(3)	5(3)	1(3)
C(26)	25(3)	20(3)	29(4)	4(3)	-1(3)	4(3)
C(27)	24(3)	18(3)	24(3)	0(3)	0(3)	-1(3)
C(28)	37(4)	44(4)	27(4)	-5(3)	-1(3)	-8(3)
C(29)	29(4)	41(4)	31(4)	-1(3)	5(3)	0(3)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for iroac3m_Pbca.

	x	y	z	U(eq)
H(4)	8144	10622	4372	25
H(7A)	7303	11633	4826	36
H(7B)	6565	11324	4668	36
H(7C)	6932	12291	4306	36
H(8A)	8891	8434	3674	38
H(8B)	9012	9479	4106	38
H(8C)	9094	9624	3403	38
H(10A)	4793	11442	3585	28
H(10B)	4871	10249	3913	28
H(12A)	4799	8849	2550	34
H(12B)	4243	9538	2890	34
H(12C)	4711	8711	3253	34
H(13A)	5430	11656	2594	35
H(13B)	4690	11305	2468	35
H(13C)	5272	10653	2144	35
H(15A)	8293	6217	2381	26
H(15B)	8614	7003	1878	26
H(17A)	7161	5850	2336	36
H(17B)	7347	5656	1652	36
H(17C)	6725	6399	1823	36
H(18A)	7172	8026	1232	40
H(18B)	7809	7326	1057	40
H(18C)	7880	8512	1384	40
H(20A)	6050	9025	674	47
H(20B)	5470	9761	945	47
H(20C)	5394	8429	892	47
H(21A)	6215	6780	3092	21
H(21B)	6871	7211	3394	21
H(23)	6828	8307	4316	24
H(25)	5124	8380	5221	34

H(27)	5201	7008	3588	27
H(28A)	6186	9743	5426	54
H(28B)	6837	9069	5265	54
H(28C)	6321	8544	5721	54
H(29A)	4248	6978	4832	51
H(29B)	4219	6836	4125	51
H(29C)	4072	8030	4421	51

Table S15. Torsion angles [°] for iroac3m_Pbca.

C(6)-C(1)-C(2)-C(3)	-0.3(8)	Ir(1)-N(1)-C(11)-C(10)	170.3(5)
Ir(1)-C(1)-C(2)-C(3)	175.2(4)	C(9)-N(1)-C(11)-C(12)	-141.1(5)
C(6)-C(1)-C(2)-C(9)	-177.5(5)	Ir(1)-N(1)-C(11)-C(12)	50.7(7)
Ir(1)-C(1)-C(2)-C(9)	-2.1(6)	O(1)-C(10)-C(11)-N(1)	26.5(5)
C(1)-C(2)-C(3)-C(4)	-1.0(8)	O(1)-C(10)-C(11)-C(13)	-89.5(6)
C(9)-C(2)-C(3)-C(4)	175.5(6)	O(1)-C(10)-C(11)-C(12)	144.8(5)
C(1)-C(2)-C(3)-C(7)	179.4(6)	C(16)-N(2)-C(14)-O(2)	-3.4(7)
C(9)-C(2)-C(3)-C(7)	-4.0(10)	Ir(1)-N(2)-C(14)-O(2)	176.8(4)
C(2)-C(3)-C(4)-C(5)	2.1(9)	C(16)-N(2)-C(14)-C(6)	177.3(5)
C(7)-C(3)-C(4)-C(5)	-178.3(6)	Ir(1)-N(2)-C(14)-C(6)	-2.5(7)
C(3)-C(4)-C(5)-C(6)	-1.9(9)	C(15)-O(2)-C(14)-N(2)	-7.8(7)
C(3)-C(4)-C(5)-C(8)	178.6(6)	C(15)-O(2)-C(14)-C(6)	171.5(6)
C(2)-C(1)-C(6)-C(5)	0.5(9)	C(1)-C(6)-C(14)-N(2)	-1.5(8)
Ir(1)-C(1)-C(6)-C(5)	-174.9(4)	C(5)-C(6)-C(14)-N(2)	178.7(6)
C(2)-C(1)-C(6)-C(14)	-179.2(5)	C(1)-C(6)-C(14)-O(2)	179.2(5)
Ir(1)-C(1)-C(6)-C(14)	5.3(7)	C(5)-C(6)-C(14)-O(2)	-0.5(10)
C(4)-C(5)-C(6)-C(1)	0.5(8)	C(14)-O(2)-C(15)-C(16)	14.8(6)
C(8)-C(5)-C(6)-C(1)	180.0(6)	C(14)-N(2)-C(16)-C(18)	-107.6(6)
C(4)-C(5)-C(6)-C(14)	-179.9(6)	Ir(1)-N(2)-C(16)-C(18)	72.2(7)
C(8)-C(5)-C(6)-C(14)	-0.4(10)	C(14)-N(2)-C(16)-C(17)	129.1(5)
C(11)-N(1)-C(9)-O(1)	8.5(7)	Ir(1)-N(2)-C(16)-C(17)	-51.2(7)
Ir(1)-N(1)-C(9)-O(1)	-179.9(4)	C(14)-N(2)-C(16)-C(15)	12.2(6)
C(11)-N(1)-C(9)-C(2)	-172.7(5)	Ir(1)-N(2)-C(16)-C(15)	-168.1(5)
Ir(1)-N(1)-C(9)-C(2)	-1.2(7)	O(2)-C(15)-C(16)-N(2)	-16.0(6)
C(10)-O(1)-C(9)-N(1)	9.6(7)	O(2)-C(15)-C(16)-C(18)	101.8(6)
C(10)-O(1)-C(9)-C(2)	-169.1(6)	O(2)-C(15)-C(16)-C(17)	-131.6(5)
C(3)-C(2)-C(9)-N(1)	-174.8(6)	Ir(1)-O(3)-C(19)-O(4)	0.7(6)
C(1)-C(2)-C(9)-N(1)	2.0(7)	Ir(1)-O(3)-C(19)-C(20)	-179.0(6)
C(3)-C(2)-C(9)-O(1)	3.8(10)	Ir(1)-O(4)-C(19)-O(3)	-0.7(6)
C(1)-C(2)-C(9)-O(1)	-179.3(5)	Ir(1)-O(4)-C(19)-C(20)	179.0(5)
C(9)-O(1)-C(10)-C(11)	-22.9(6)	Ir(1)-C(21)-C(22)-C(27)	94.3(6)
C(9)-N(1)-C(11)-C(13)	96.5(6)	Ir(1)-C(21)-C(22)-C(23)	-86.4(6)
Ir(1)-N(1)-C(11)-C(13)	-71.7(7)	C(27)-C(22)-C(23)-C(24)	-4.5(9)
C(9)-N(1)-C(11)-C(10)	-21.5(6)	C(21)-C(22)-C(23)-C(24)	176.2(6)

C(22)-C(23)-C(24)-C(25)	1.9(9)	C(24)-C(25)-C(26)-C(29)	178.5(6)
C(22)-C(23)-C(24)-C(28)	-178.2(6)	C(23)-C(22)-C(27)-C(26)	4.1(9)
C(23)-C(24)-C(25)-C(26)	1.2(10)	C(21)-C(22)-C(27)-C(26)	-176.6(6)
C(28)-C(24)-C(25)-C(26)	-178.6(6)	C(25)-C(26)-C(27)-C(22)	-1.1(9)
C(24)-C(25)-C(26)-C(27)	-1.7(9)	C(29)-C(26)-C(27)-C(22)	178.7(6)

3. (Phebox)Ir(mesityl)($OCOCF_3$) **(4)**

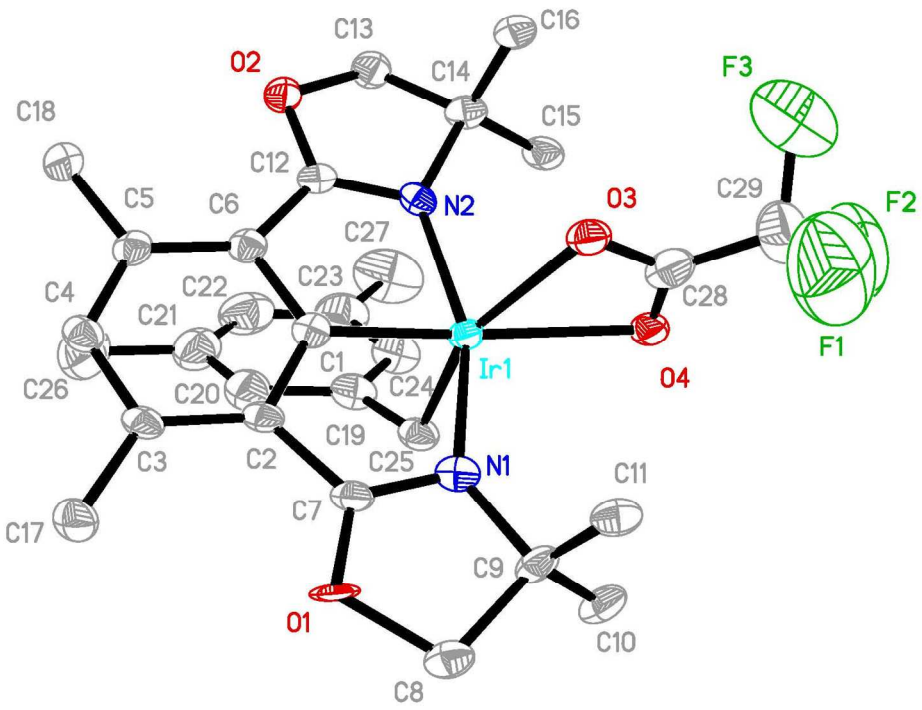


Table S16. Crystal data and structure refinement for irme_Pbca.

Identification code	irme_Pbca	
Empirical formula	C29 H34 F3 Ir N2 O4	
Formula weight	723.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 20.8528(8) Å	α= 90°.
	b = 11.8997(5) Å	β= 90°.
	c = 22.6610(9) Å	γ = 90°.
Volume	5623.1(4) $Å^3$	
Z	8	
Density (calculated)	1.710 Mg/m^3	
Absorption coefficient	4.806 mm^{-1}	

F(000)	2864
Crystal size	0.200 x 0.070 x 0.020 mm^3
Theta range for data collection	2.046 to 24.163°.
Index ranges	-24<=h<=24, -13<=k<=13, -26<=l<=26
Reflections collected	43719
Independent reflections	4487 [R(int) = 0.1391]
Completeness to theta = 24.163°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7451 and 0.5124
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4487 / 560 / 360
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1303
R indices (all data)	R1 = 0.0879, wR2 = 0.1436
Extinction coefficient	n/a
Largest diff. peak and hole	2.358 and -1.692 e.$Å^{-3}$

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for irme_Pbca. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	6503(1)	5956(1)	7386(1)	18(1)
N(1)	7366(4)	6660(7)	7624(4)	22(2)
N(2)	5869(4)	4914(7)	6952(4)	19(2)
O(1)	8405(3)	6772(6)	7387(4)	25(2)
O(2)	5739(3)	3642(6)	6217(3)	24(2)
O(3)	6384(4)	5026(6)	8275(3)	25(2)
O(4)	5873(3)	6638(6)	8138(3)	25(2)
F(1)	6169(7)	5742(15)	9464(6)	135(4)
F(2)	5315(7)	6412(12)	9192(6)	122(4)
F(3)	5442(7)	4730(12)	9145(6)	134(4)
C(1)	7070(5)	5241(9)	6824(5)	18(2)
C(2)	7714(5)	5553(9)	6807(5)	19(2)
C(3)	8120(5)	5129(9)	6364(5)	21(2)
C(4)	7845(5)	4366(9)	5964(5)	23(2)
C(5)	7216(5)	4021(9)	5977(5)	21(2)
C(6)	6812(5)	4460(9)	6416(5)	20(2)
C(7)	7840(5)	6351(9)	7275(5)	22(2)
C(8)	8287(5)	7701(10)	7828(5)	27(2)
C(9)	7608(5)	7440(10)	8077(5)	24(2)
C(10)	7190(6)	8482(10)	8093(6)	29(3)
C(11)	7640(5)	6836(10)	8665(5)	27(3)
C(12)	6127(5)	4341(9)	6525(5)	21(2)
C(13)	5097(5)	3951(10)	6417(5)	27(2)
C(14)	5192(5)	4504(10)	7018(5)	23(2)
C(15)	4719(5)	5477(10)	7133(6)	27(2)
C(16)	5172(6)	3659(10)	7504(5)	27(3)
C(17)	8820(5)	5425(10)	6305(5)	27(3)
C(18)	6965(6)	3178(10)	5529(5)	31(3)
C(19)	6130(6)	7028(11)	6189(5)	30(2)
C(20)	6483(7)	6581(11)	5713(6)	38(2)
C(21)	6171(8)	6347(12)	5190(6)	45(3)

C(22)	5537(8)	6543(13)	5142(7)	51(3)
C(23)	5179(7)	6985(12)	5580(6)	46(3)
C(24)	5479(6)	7234(11)	6102(6)	37(2)
C(25)	6446(5)	7250(9)	6772(5)	25(2)
C(26)	6571(9)	5900(14)	4675(7)	70(4)
C(27)	4458(7)	7197(16)	5505(8)	72(4)
C(28)	6006(6)	5806(11)	8463(6)	32(2)
C(29)	5752(8)	5711(14)	9042(7)	55(3)

Table S18. Bond lengths [Å] and angles [°] for irme_Pbca.

Ir(1)-C(1)	1.936(11)	C(9)-C(10)	1.516(15)
Ir(1)-N(1)	2.057(9)	C(10)-H(10A)	0.9800
Ir(1)-N(2)	2.062(9)	C(10)-H(10B)	0.9800
Ir(1)-C(25)	2.080(11)	C(10)-H(10C)	0.9800
Ir(1)-O(4)	2.299(7)	C(11)-H(11A)	0.9800
Ir(1)-O(3)	2.310(8)	C(11)-H(11B)	0.9800
N(1)-C(7)	1.316(14)	C(11)-H(11C)	0.9800
N(1)-C(9)	1.474(14)	C(13)-C(14)	1.524(16)
N(2)-C(12)	1.299(14)	C(13)-H(13A)	0.9900
N(2)-C(14)	1.503(13)	C(13)-H(13B)	0.9900
O(1)-C(7)	1.306(13)	C(14)-C(16)	1.493(16)
O(1)-C(8)	1.510(13)	C(14)-C(15)	1.541(15)
O(2)-C(12)	1.354(13)	C(15)-H(15A)	0.9800
O(2)-C(13)	1.462(13)	C(15)-H(15B)	0.9800
O(3)-C(28)	1.290(14)	C(15)-H(15C)	0.9800
O(4)-C(28)	1.264(15)	C(16)-H(16A)	0.9800
F(1)-C(29)	1.29(2)	C(16)-H(16B)	0.9800
F(2)-C(29)	1.281(18)	C(16)-H(16C)	0.9800
F(3)-C(29)	1.354(19)	C(17)-H(17A)	0.9800
C(1)-C(2)	1.394(15)	C(17)-H(17B)	0.9800
C(1)-C(6)	1.416(15)	C(17)-H(17C)	0.9800
C(2)-C(3)	1.405(15)	C(18)-H(18A)	0.9800
C(2)-C(7)	1.448(15)	C(18)-H(18B)	0.9800
C(3)-C(4)	1.404(15)	C(18)-H(18C)	0.9800
C(3)-C(17)	1.507(15)	C(19)-C(24)	1.394(17)
C(4)-C(5)	1.376(15)	C(19)-C(20)	1.411(18)
C(4)-H(4)	0.9500	C(19)-C(25)	1.497(16)
C(5)-C(6)	1.404(15)	C(20)-C(21)	1.382(19)
C(5)-C(18)	1.521(15)	C(20)-H(20)	0.9500
C(6)-C(12)	1.456(15)	C(21)-C(22)	1.35(2)
C(8)-C(9)	1.556(15)	C(21)-C(26)	1.53(2)
C(8)-H(8A)	0.9900	C(22)-C(23)	1.35(2)
C(8)-H(8B)	0.9900	C(22)-H(22)	0.9500
C(9)-C(11)	1.515(16)	C(23)-C(24)	1.371(18)

C(23)-C(27)	1.53(2)	C(26)-H(26C)	0.9800
C(24)-H(24)	0.9500	C(27)-H(27A)	0.9800
C(25)-H(25A)	0.9900	C(27)-H(27B)	0.9800
C(25)-H(25B)	0.9900	C(27)-H(27C)	0.9800
C(26)-H(26A)	0.9800	C(28)-C(29)	1.42(2)
C(26)-H(26B)	0.9800		

C(1)-Ir(1)-N(1)	79.4(4)	C(1)-C(2)-C(7)	109.2(10)
C(1)-Ir(1)-N(2)	79.2(4)	C(3)-C(2)-C(7)	130.6(10)
N(1)-Ir(1)-N(2)	158.5(4)	C(4)-C(3)-C(2)	116.6(10)
C(1)-Ir(1)-C(25)	85.4(4)	C(4)-C(3)-C(17)	119.2(10)
N(1)-Ir(1)-C(25)	85.6(4)	C(2)-C(3)-C(17)	124.2(10)
N(2)-Ir(1)-C(25)	95.1(4)	C(5)-C(4)-C(3)	124.6(11)
C(1)-Ir(1)-O(4)	172.8(4)	C(5)-C(4)-H(4)	117.7
N(1)-Ir(1)-O(4)	99.3(3)	C(3)-C(4)-H(4)	117.7
N(2)-Ir(1)-O(4)	101.5(3)	C(4)-C(5)-C(6)	118.5(11)
C(25)-Ir(1)-O(4)	101.6(4)	C(4)-C(5)-C(18)	120.7(10)
C(1)-Ir(1)-O(3)	115.4(4)	C(6)-C(5)-C(18)	120.8(10)
N(1)-Ir(1)-O(3)	93.5(3)	C(5)-C(6)-C(1)	118.5(10)
N(2)-Ir(1)-O(3)	93.4(3)	C(5)-C(6)-C(12)	132.3(11)
C(25)-Ir(1)-O(3)	158.7(4)	C(1)-C(6)-C(12)	109.0(10)
O(4)-Ir(1)-O(3)	57.5(3)	O(1)-C(7)-N(1)	116.9(10)
C(7)-N(1)-C(9)	109.8(9)	O(1)-C(7)-C(2)	123.8(10)
C(7)-N(1)-Ir(1)	112.7(7)	N(1)-C(7)-C(2)	119.2(10)
C(9)-N(1)-Ir(1)	137.5(7)	O(1)-C(8)-C(9)	104.1(8)
C(12)-N(2)-C(14)	107.0(9)	O(1)-C(8)-H(8A)	110.9
C(12)-N(2)-Ir(1)	114.0(7)	C(9)-C(8)-H(8A)	110.9
C(14)-N(2)-Ir(1)	138.6(7)	O(1)-C(8)-H(8B)	110.9
C(7)-O(1)-C(8)	105.2(8)	C(9)-C(8)-H(8B)	110.9
C(12)-O(2)-C(13)	103.4(8)	H(8A)-C(8)-H(8B)	109.0
C(28)-O(3)-Ir(1)	90.5(7)	N(1)-C(9)-C(11)	109.2(9)
C(28)-O(4)-Ir(1)	91.7(7)	N(1)-C(9)-C(10)	109.6(9)
C(2)-C(1)-C(6)	121.6(10)	C(11)-C(9)-C(10)	113.1(10)
C(2)-C(1)-Ir(1)	119.3(8)	N(1)-C(9)-C(8)	100.6(9)
C(6)-C(1)-Ir(1)	119.0(8)	C(11)-C(9)-C(8)	112.0(9)
C(1)-C(2)-C(3)	120.2(10)	C(10)-C(9)-C(8)	111.6(10)

C(9)-C(10)-H(10A)	109.5	C(14)-C(16)-H(16C)	109.5
C(9)-C(10)-H(10B)	109.5	H(16A)-C(16)-H(16C)	109.5
H(10A)-C(10)-H(10B)	109.5	H(16B)-C(16)-H(16C)	109.5
C(9)-C(10)-H(10C)	109.5	C(3)-C(17)-H(17A)	109.5
H(10A)-C(10)-H(10C)	109.5	C(3)-C(17)-H(17B)	109.5
H(10B)-C(10)-H(10C)	109.5	H(17A)-C(17)-H(17B)	109.5
C(9)-C(11)-H(11A)	109.5	C(3)-C(17)-H(17C)	109.5
C(9)-C(11)-H(11B)	109.5	H(17A)-C(17)-H(17C)	109.5
H(11A)-C(11)-H(11B)	109.5	H(17B)-C(17)-H(17C)	109.5
C(9)-C(11)-H(11C)	109.5	C(5)-C(18)-H(18A)	109.5
H(11A)-C(11)-H(11C)	109.5	C(5)-C(18)-H(18B)	109.5
H(11B)-C(11)-H(11C)	109.5	H(18A)-C(18)-H(18B)	109.5
N(2)-C(12)-O(2)	117.4(10)	C(5)-C(18)-H(18C)	109.5
N(2)-C(12)-C(6)	118.7(10)	H(18A)-C(18)-H(18C)	109.5
O(2)-C(12)-C(6)	123.9(10)	H(18B)-C(18)-H(18C)	109.5
O(2)-C(13)-C(14)	105.5(9)	C(24)-C(19)-C(20)	117.8(12)
O(2)-C(13)-H(13A)	110.6	C(24)-C(19)-C(25)	121.4(11)
C(14)-C(13)-H(13A)	110.6	C(20)-C(19)-C(25)	120.8(11)
O(2)-C(13)-H(13B)	110.6	C(21)-C(20)-C(19)	119.2(13)
C(14)-C(13)-H(13B)	110.6	C(21)-C(20)-H(20)	120.4
H(13A)-C(13)-H(13B)	108.8	C(19)-C(20)-H(20)	120.4
C(16)-C(14)-N(2)	108.5(9)	C(22)-C(21)-C(20)	119.8(14)
C(16)-C(14)-C(13)	111.4(10)	C(22)-C(21)-C(26)	122.3(15)
N(2)-C(14)-C(13)	100.0(9)	C(20)-C(21)-C(26)	117.8(15)
C(16)-C(14)-C(15)	111.3(10)	C(23)-C(22)-C(21)	123.5(14)
N(2)-C(14)-C(15)	112.0(9)	C(23)-C(22)-H(22)	118.2
C(13)-C(14)-C(15)	113.1(9)	C(21)-C(22)-H(22)	118.2
C(14)-C(15)-H(15A)	109.5	C(22)-C(23)-C(24)	117.8(14)
C(14)-C(15)-H(15B)	109.5	C(22)-C(23)-C(27)	121.7(14)
H(15A)-C(15)-H(15B)	109.5	C(24)-C(23)-C(27)	120.5(14)
C(14)-C(15)-H(15C)	109.5	C(23)-C(24)-C(19)	122.0(13)
H(15A)-C(15)-H(15C)	109.5	C(23)-C(24)-H(24)	119.0
H(15B)-C(15)-H(15C)	109.5	C(19)-C(24)-H(24)	119.0
C(14)-C(16)-H(16A)	109.5	C(19)-C(25)-Ir(1)	119.0(8)
C(14)-C(16)-H(16B)	109.5	C(19)-C(25)-H(25A)	107.6
H(16A)-C(16)-H(16B)	109.5	Ir(1)-C(25)-H(25A)	107.6

C(19)-C(25)-H(25B)	107.6	C(23)-C(27)-H(27C)	109.5
Ir(1)-C(25)-H(25B)	107.6	H(27A)-C(27)-H(27C)	109.5
H(25A)-C(25)-H(25B)	107.0	H(27B)-C(27)-H(27C)	109.5
C(21)-C(26)-H(26A)	109.5	O(4)-C(28)-O(3)	120.3(11)
C(21)-C(26)-H(26B)	109.5	O(4)-C(28)-C(29)	121.2(12)
H(26A)-C(26)-H(26B)	109.5	O(3)-C(28)-C(29)	118.5(13)
C(21)-C(26)-H(26C)	109.5	F(2)-C(29)-F(1)	105.3(15)
H(26A)-C(26)-H(26C)	109.5	F(2)-C(29)-F(3)	100.2(14)
H(26B)-C(26)-H(26C)	109.5	F(1)-C(29)-F(3)	102.6(16)
C(23)-C(27)-H(27A)	109.5	F(2)-C(29)-C(28)	117.3(15)
C(23)-C(27)-H(27B)	109.5	F(1)-C(29)-C(28)	115.4(15)
H(27A)-C(27)-H(27B)	109.5	F(3)-C(29)-C(28)	114.0(14)

Table S19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for irme_Pbca. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	16(1)	14(1)	24(1)	-2(1)	1(1)	-1(1)
N(1)	20(4)	19(4)	28(4)	3(3)	-3(3)	-2(3)
N(2)	16(3)	19(4)	21(4)	5(3)	0(3)	0(3)
O(1)	24(3)	11(3)	39(4)	-3(3)	0(3)	-12(3)
O(2)	21(3)	25(4)	27(4)	-5(3)	0(3)	-4(3)
O(3)	27(4)	18(4)	30(4)	0(3)	0(3)	-3(3)
O(4)	18(4)	20(4)	37(4)	-7(3)	8(3)	-3(3)
F(1)	130(8)	195(11)	81(7)	4(8)	-15(6)	-3(7)
F(2)	131(8)	125(7)	109(8)	0(7)	49(6)	32(7)
F(3)	160(10)	112(7)	131(9)	9(7)	55(7)	-40(7)
C(1)	17(4)	14(4)	23(4)	5(3)	-3(3)	5(3)
C(2)	18(4)	14(4)	26(4)	5(3)	0(3)	-1(3)
C(3)	21(4)	15(4)	27(4)	8(3)	2(3)	-1(4)
C(4)	23(4)	19(4)	26(5)	6(3)	2(4)	0(4)
C(5)	21(4)	15(4)	28(4)	1(4)	-1(3)	3(4)
C(6)	20(3)	15(4)	25(4)	2(3)	-1(3)	2(3)
C(7)	19(4)	15(4)	30(4)	2(3)	1(3)	-4(3)
C(8)	23(4)	23(4)	34(5)	-3(4)	-6(4)	-3(4)
C(9)	22(4)	23(4)	27(4)	-9(3)	-6(4)	-4(4)
C(10)	31(6)	18(5)	39(7)	-9(5)	-4(5)	0(5)
C(11)	23(6)	26(6)	31(5)	-2(4)	-7(5)	-7(5)
C(12)	22(3)	16(4)	24(4)	2(3)	-2(3)	-3(3)
C(13)	22(4)	28(5)	31(4)	-3(4)	0(4)	-3(4)
C(14)	15(4)	24(4)	29(4)	-1(4)	-6(3)	-5(3)
C(15)	17(5)	25(5)	37(6)	0(5)	2(5)	-5(4)
C(16)	29(6)	24(5)	29(6)	-4(4)	-1(5)	-8(5)
C(17)	18(5)	25(6)	37(7)	1(5)	2(5)	2(5)
C(18)	29(6)	26(6)	38(7)	-7(5)	7(5)	-4(5)
C(19)	30(4)	27(4)	34(4)	6(4)	-3(4)	-5(4)
C(20)	45(5)	32(5)	36(4)	4(4)	3(4)	-6(5)
C(21)	66(5)	33(5)	35(5)	2(4)	2(4)	-7(5)

C(22)	67(5)	44(5)	41(5)	2(4)	-13(4)	-17(5)
C(23)	48(5)	47(5)	43(5)	7(5)	-13(4)	-11(5)
C(24)	36(4)	39(5)	37(5)	6(4)	-5(4)	-5(5)
C(25)	23(5)	17(5)	34(5)	4(4)	4(4)	0(4)
C(26)	111(10)	52(8)	48(7)	-1(7)	21(7)	-7(8)
C(27)	57(6)	85(10)	75(9)	20(8)	-31(6)	-13(8)
C(28)	29(4)	26(4)	43(4)	-8(4)	-2(4)	-3(4)
C(29)	57(6)	57(6)	49(5)	-3(5)	16(4)	1(5)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for irme_Pbca.

	x	y	z	U(eq)
H(4)	8113	4067	5664	27
H(8A)	8296	8446	7633	32
H(8B)	8613	7688	8146	32
H(10A)	7127	8762	7690	44
H(10B)	7399	9063	8331	44
H(10C)	6773	8295	8266	44
H(11A)	7918	6176	8629	40
H(11B)	7208	6597	8781	40
H(11C)	7814	7345	8965	40
H(13A)	4822	3277	6453	32
H(13B)	4894	4482	6137	32
H(15A)	4282	5180	7155	40
H(15B)	4748	6023	6810	40
H(15C)	4829	5845	7506	40
H(16A)	5282	4025	7879	41
H(16B)	5480	3058	7423	41
H(16C)	4739	3340	7532	41
H(17A)	9064	5045	6616	40
H(17B)	8873	6240	6344	40
H(17C)	8976	5182	5918	40
H(18A)	6585	3488	5332	46
H(18B)	6849	2478	5730	46
H(18C)	7298	3024	5235	46
H(20)	6930	6442	5752	45
H(22)	5332	6360	4780	61
H(24)	5236	7557	6414	45
H(25A)	6215	7883	6960	29
H(25B)	6888	7511	6691	29
H(26A)	6399	5174	4546	106
H(26B)	7017	5804	4803	106

H(26C)	6555	6435	4347	106
H(27A)	4366	7371	5091	109
H(27B)	4329	7832	5754	109
H(27C)	4220	6524	5623	109

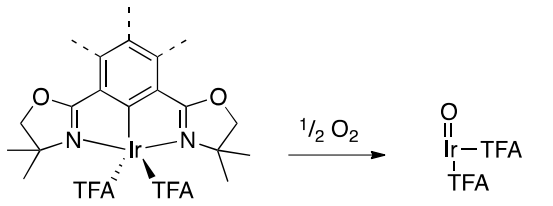
Table S21. Torsion angles [°] for irme_Pbca.

C(6)-C(1)-C(2)-C(3)	2.7(16)	Ir(1)-N(1)-C(9)-C(10)	-49.7(14)
Ir(1)-C(1)-C(2)-C(3)	-173.6(8)	C(7)-N(1)-C(9)-C(8)	11.5(11)
C(6)-C(1)-C(2)-C(7)	-179.6(10)	Ir(1)-N(1)-C(9)-C(8)	-167.4(8)
Ir(1)-C(1)-C(2)-C(7)	4.1(12)	O(1)-C(8)-C(9)-N(1)	-17.1(10)
C(1)-C(2)-C(3)-C(4)	-2.0(15)	O(1)-C(8)-C(9)-C(11)	98.7(10)
C(7)-C(2)-C(3)-C(4)	-179.1(11)	O(1)-C(8)-C(9)-C(10)	-133.3(9)
C(1)-C(2)-C(3)-C(17)	179.4(10)	C(14)-N(2)-C(12)-O(2)	6.4(13)
C(7)-C(2)-C(3)-C(17)	2.3(19)	Ir(1)-N(2)-C(12)-O(2)	-179.6(7)
C(2)-C(3)-C(4)-C(5)	0.4(16)	C(14)-N(2)-C(12)-C(6)	-172.0(9)
C(17)-C(3)-C(4)-C(5)	179.1(11)	Ir(1)-N(2)-C(12)-C(6)	2.1(13)
C(3)-C(4)-C(5)-C(6)	0.4(17)	C(13)-O(2)-C(12)-N(2)	10.7(13)
C(3)-C(4)-C(5)-C(18)	-179.3(10)	C(13)-O(2)-C(12)-C(6)	-171.1(10)
C(4)-C(5)-C(6)-C(1)	0.2(16)	C(5)-C(6)-C(12)-N(2)	-175.6(11)
C(18)-C(5)-C(6)-C(1)	179.9(10)	C(1)-C(6)-C(12)-N(2)	-0.7(14)
C(4)-C(5)-C(6)-C(12)	174.7(11)	C(5)-C(6)-C(12)-O(2)	6.2(19)
C(18)-C(5)-C(6)-C(12)	-5.6(19)	C(1)-C(6)-C(12)-O(2)	-178.9(10)
C(2)-C(1)-C(6)-C(5)	-1.8(16)	C(12)-O(2)-C(13)-C(14)	-22.6(11)
Ir(1)-C(1)-C(6)-C(5)	174.5(8)	C(12)-N(2)-C(14)-C(16)	97.3(11)
C(2)-C(1)-C(6)-C(12)	-177.4(10)	Ir(1)-N(2)-C(14)-C(16)	-74.5(13)
Ir(1)-C(1)-C(6)-C(12)	-1.2(12)	C(12)-N(2)-C(14)-C(13)	-19.4(11)
C(8)-O(1)-C(7)-N(1)	-11.7(13)	Ir(1)-N(2)-C(14)-C(13)	168.8(8)
C(8)-O(1)-C(7)-C(2)	170.1(10)	C(12)-N(2)-C(14)-C(15)	-139.5(10)
C(9)-N(1)-C(7)-O(1)	-0.3(14)	Ir(1)-N(2)-C(14)-C(15)	48.7(14)
Ir(1)-N(1)-C(7)-O(1)	178.9(7)	O(2)-C(13)-C(14)-C(16)	-89.3(11)
C(9)-N(1)-C(7)-C(2)	178.1(9)	O(2)-C(13)-C(14)-N(2)	25.3(11)
Ir(1)-N(1)-C(7)-C(2)	-2.7(13)	O(2)-C(13)-C(14)-C(15)	144.5(9)
C(1)-C(2)-C(7)-O(1)	177.6(10)	C(24)-C(19)-C(20)-C(21)	-1.3(19)
C(3)-C(2)-C(7)-O(1)	-5.1(19)	C(25)-C(19)-C(20)-C(21)	177.5(12)
C(1)-C(2)-C(7)-N(1)	-0.6(14)	C(19)-C(20)-C(21)-C(22)	0(2)
C(3)-C(2)-C(7)-N(1)	176.7(11)	C(19)-C(20)-C(21)-C(26)	178.0(12)
C(7)-O(1)-C(8)-C(9)	17.8(11)	C(20)-C(21)-C(22)-C(23)	1(2)
C(7)-N(1)-C(9)-C(11)	-106.4(11)	C(26)-C(21)-C(22)-C(23)	-176.9(14)
Ir(1)-N(1)-C(9)-C(11)	74.7(13)	C(21)-C(22)-C(23)-C(24)	-1(2)
C(7)-N(1)-C(9)-C(10)	129.2(10)	C(21)-C(22)-C(23)-C(27)	179.8(15)

C(22)-C(23)-C(24)-C(19)	-1(2)
C(27)-C(23)-C(24)-C(19)	178.5(13)
C(20)-C(19)-C(24)-C(23)	1.9(19)
C(25)-C(19)-C(24)-C(23)	-176.9(12)
C(24)-C(19)-C(25)-Ir(1)	92.2(13)
C(20)-C(19)-C(25)-Ir(1)	-86.6(13)
Ir(1)-O(4)-C(28)-O(3)	0.1(11)
Ir(1)-O(4)-C(28)-C(29)	179.4(12)
Ir(1)-O(3)-C(28)-O(4)	-0.1(11)
Ir(1)-O(3)-C(28)-C(29)	-179.4(12)
O(4)-C(28)-C(29)-F(2)	10(2)
O(3)-C(28)-C(29)-F(2)	-171.2(14)
O(4)-C(28)-C(29)-F(1)	-115.4(17)
O(3)-C(28)-C(29)-F(1)	64(2)
O(4)-C(28)-C(29)-F(3)	126.2(15)
O(3)-C(28)-C(29)-F(3)	-55(2)

Comparison between mono-*p*-methyl Phebox and bis-*m*-methyl Phebox ligands

Calculations by DFT reported in this manuscript were completed on mono-*p*-methyl Phebox, while experimentally bis-*m*-methyl Phebox was synthesized. In order to justify this choice, the two-electron oxidation of the non-aquo ground state (**2b**) by ½ equivalent of O_2 was compared. Scheme **S1** shows the results. The two complexes are 0.7 kcal/mol different in energy, which is less than the error of DFT. Thus we feel comfortable in our substitution of the complexes.



2b: 0.0 kcal/mol

m-CH_3: 0.37
p-CH_3: -0.35

Scheme S1: Substitution of the *m*-CH_3 is not significantly different from the *p*-CH_3 complex.

Geometries for DFT Calculations

Formats can be directly imported as .xyz files.

1a

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Ir1	-0.2277638465	-1.1816906715	1.6993797860
C2	0.2907558468	-3.1766726083	3.6740575702
O3	1.0018654355	-3.9862664359	4.4686755070
N4	0.9730527002	-2.3890044803	2.8897473932
C5	-3.8919091350	-2.7518228914	3.0971831730
C6	-3.4895146507	-3.7016671817	4.0528968224
C7	-2.1191142009	-3.8955986759	4.3112022351

C8	-1.1641506318	-3.1350865477	3.6295788905
C9	-1.5730837819	-2.1735855439	2.6926988543
C10	-2.9326766584	-1.9870036395	2.4220990547
C11	-3.0857426091	-0.9731813041	1.3911726887
N12	-2.0336379738	-0.3783596171	0.8881408432
O13	-4.2782689475	-0.5884974181	0.9118297640
C14	3.0469931366	-3.1135421185	1.7756292338
H15	-4.9499785074	-2.6192700889	2.8850918395
H16	-1.8107477778	-4.6456825015	5.0358863283
H17	4.1132472962	-3.3218077228	1.9192287624
H18	2.9403954289	-2.3530682611	0.9984058132
C19	-1.7290306946	0.7668030430	-1.3257354519
O20	-0.1596739962	0.2570828975	3.2088946524
O21	0.5808652097	-1.5328674148	-1.4497887185
H22	2.5532366741	-4.0293026714	1.4363517446
H23	-1.7009129404	-0.2051887105	-1.8218918671
H24	-0.6974493613	1.0740705758	-1.1416047126
H25	-2.1859390453	1.4999959304	-2.0000959264
C26	0.1253687023	2.3628082727	4.2353930345
H27	-0.8889493563	2.7773747113	4.2650350273
H28	0.2799072629	1.7954430888	5.1555130566
H29	0.8332858023	3.1906508093	4.1691388475
C30	-0.1655294516	-3.7865060061	-1.8096291209
H31	0.1799253958	-3.6069612702	-2.8284358733
H32	0.3612983123	-4.6466323920	-1.3853155077

H33	-1.2318548529	-4.0335144687	-1.8166186548
C34	-4.5239119882	-4.5039236965	4.8121625956
H35	-4.1525849317	-5.5035600929	5.0592143627
H36	-4.7951707736	-4.0157937123	5.7568697603
H37	-5.4438785959	-4.6215602013	4.2314422334
C38	2.4224217623	-2.6093581646	3.0841317157
C39	-2.5114738905	0.7130196759	-0.0149677399
C40	3.0894278553	-1.3080804193	3.5483588489
H41	2.9932060783	-0.5461820551	2.7712920119
H42	2.6182948595	-0.9340316246	4.4622793398
H43	4.1542761205	-1.4762662964	3.7446664293
C44	-2.4396123129	2.0584671150	0.7274076935
H45	-2.8270716747	2.8575081488	0.0848418961
H46	-3.0428618505	2.0308071589	1.6413722897
H47	-1.4078528054	2.2941601262	0.9961489173
C48	-3.9826593356	0.2727757616	-0.2247575311
C49	2.4083558772	-3.7039841014	4.1996308266
H50	2.8595899911	-3.3650454176	5.1362460313
H51	2.8772747961	-4.6406917706	3.8869316913
H52	-4.1163665210	-0.3233436678	-1.1350025266
H53	-4.6965311676	1.0981563791	-0.2142850036
C54	0.2555425901	1.4669663777	3.0122433378
O55	0.6987079278	1.9381451982	1.9463925853
C56	0.0767388515	-2.5540912224	-0.9485489077
O57	-0.2920486878	-2.7116996848	0.2838471116

O58	1.4482244008	-0.1610020966	0.5914001211
H59	1.1823187384	-0.4266196067	-0.3276153088
H60	1.2200949676	0.7742328557	0.8277122525

1b

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Ir1	-0.3637553040	-1.2752589230	1.6097348493
C2	0.2622399201	-3.1725698992	3.6507755687
O3	1.0046138681	-3.9229961076	4.4756992912
N4	0.9120327931	-2.4460412385	2.7822194216
C5	-3.9372266054	-2.6250277024	3.3505003194
C6	-3.4968971438	-3.5497875590	4.3151046527
C7	-2.1197721251	-3.7912898867	4.4751291166
C8	-1.1900860990	-3.1125659250	3.6803629023
C9	-1.6397633309	-2.1943973519	2.7183510780
C10	-3.0108676512	-1.9433810605	2.5544047628
C11	-3.2000279289	-0.9489142021	1.5109231160
N12	-2.1558043658	-0.4722044203	0.8888558715
O13	-4.3909105461	-0.4610181398	1.1386211040
C14	3.0727143379	-2.9831240309	1.6956938918
H15	-5.0021268773	-2.4425889570	3.2294667916
H16	-1.7836306676	-4.5076243742	5.2211155377
H17	4.1438739031	-3.1341072924	1.8695240723
H18	2.9479978386	-2.1875327912	0.9565421162

C19	-2.0352398403	0.3061121008	-1.4604623465
O20	-0.3541394954	0.1617726969	3.1089836360
O21	1.0457006041	-0.9956517817	-0.3740172424
H22	2.6516187708	-3.9073345682	1.2872953360
H23	-2.3625203084	-0.6761879088	-1.8155776156
H24	-0.9424537216	0.3237393977	-1.4444093578
H25	-2.3868432107	1.0673728194	-2.1656207768
C26	0.4018827145	2.2268980195	3.9867527701
H27	-0.5372496524	2.7884770925	3.9317977355
H28	0.4410894975	1.7538258387	4.9715836163
H29	1.2359643906	2.9195703159	3.8647821324
C30	0.9209527506	-2.7638455522	-2.0306149223
H31	1.6389935404	-2.1532931801	-2.5793181665
H32	1.3503624540	-3.7505161820	-1.8307847525
H33	0.0234469205	-2.9173221987	-2.6376789681
C34	-4.4998104663	-4.2599288905	5.1985231367
H35	-4.1433727167	-5.2523565666	5.4914253989
H36	-4.6898510266	-3.6970765814	6.1212936764
H37	-5.4612897117	-4.3852831139	4.6911161336
C38	2.3709240287	-2.5956833782	3.0018068415
C39	-2.5822084382	0.5874179752	-0.0569936979
C40	2.9379015273	-1.2833809342	3.5648935541
H41	2.7757477354	-0.4659652439	2.8572676363
H42	2.4480751386	-1.0227790684	4.5086595321
H43	4.0137597953	-1.3853244982	3.7472351451

C44	-2.1028892125	1.9529437216	0.4589360126
H45	-2.4200210147	2.7474244075	-0.2261942720
H46	-2.5206506827	2.1607820536	1.4493734201
H47	-1.0123447119	1.9671437664	0.5357256059
C48	-4.1331487437	0.4375952316	0.0184735029
C49	2.3901697045	-3.7484209396	4.0530513331
H50	2.9797951864	-3.5148854509	4.9422992272
H51	2.7261999656	-4.7004736436	3.6299831971
H52	-4.5568162556	-0.0259504552	-0.8781785121
H53	-4.6504358841	1.3776156314	0.2229491349
C54	0.4335170508	1.1801718781	2.8809115341
O55	1.1283905088	1.3132818106	1.8720304988
C56	0.5521287474	-2.0922039404	-0.7289685340
O57	-0.3048145845	-2.6835473486	0.0363923275

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Ir1	-0.2849057940	-0.0766101814	0.0513254554
C2	0.7075839055	-0.8896287622	2.6132903008
O3	1.5836050962	-1.2569803861	3.5530863521
N4	1.2034899039	-0.4939159662	1.4739368938
C5	-3.5316970725	-1.0655876327	2.5688676431
C6	-2.9063290710	-1.4107906982	3.7799946299
C7	-1.5021955010	-1.3597372147	3.8814757555

C8	-0.7366213845	-0.9397588341	2.7907634856
C9	-1.3684691246	-0.5623270021	1.5978689726
C10	-2.7608175506	-0.6395559094	1.4796245204
C11	-3.1526664646	-0.2822530308	0.1250003112
N12	-2.2449696780	0.0884322357	-0.7364186782
O13	-4.4143869906	-0.3453599489	-0.3177601422
C14	3.2505489153	-1.3673003378	0.3725012103
H15	-4.6132967210	-1.1380086850	2.4819828944
H16	-1.0189583147	-1.6645341345	4.8067060636
H17	4.3417533834	-1.4338980646	0.4556565156
H18	2.9990132513	-0.8882046129	-0.5773950602
C19	-2.2607364234	-0.5571253316	-3.1237887822
O20	1.0092989552	0.2185477456	-1.7661446677
H21	0.0839299181	1.8818419747	-0.3622134025
C22	-0.2033311837	2.1237467405	0.9986617329
H23	-0.0801702869	1.6250704891	1.9563452872
O24	-0.4309160765	-1.9851097329	-0.7360623379
H25	2.8220808464	-2.3715412249	0.3761521968
H26	-2.3205783244	-1.6090939731	-2.8346354452
H27	-1.2035151263	-0.3130595650	-3.2498322730
H28	-2.7745229784	-0.4156781506	-4.0817522341
H29	0.7006430289	2.7374840792	0.8954674623
C30	1.9099582870	1.7346876909	-3.3923559273
H31	2.5540817527	2.6005594343	-3.2195955893
H32	2.5016427472	0.8735316756	-3.7042550485

H33	1.2140007070	2.0005408930	-4.1954247861
C34	-0.2539112968	-4.2939843762	-1.1269782422
H35	-1.3238916355	-4.3807617113	-1.3406390533
H36	0.2592371139	-4.1489845303	-2.0830604685
H37	0.1019710742	-5.2098551838	-0.6525873179
C38	-3.7324703904	-1.8343273093	4.9750936655
H39	-3.2414406110	-2.6360219362	5.5362177731
H40	-3.8878551967	-1.0002201114	5.6714837897
H41	-4.7198969717	-2.1938117868	4.6708479696
C42	2.6848050633	-0.5496692368	1.5376317555
C43	-2.8895583253	0.3399760811	-2.0506953025
C44	3.2477057655	0.8810973433	1.5416366745
H45	2.9737933842	1.4004535720	0.6191726294
H46	2.8582224685	1.4571014955	2.3875757163
H47	4.3409094014	0.8602932244	1.6118160262
C48	-2.7761123564	1.8250810668	-2.4214922685
H49	-3.2635209841	2.0080037816	-3.3863748885
H50	-3.2505134324	2.4544518371	-1.6631484117
H51	-1.7291916939	2.1276566749	-2.4946626653
C52	-4.3680741693	-0.0587355456	-1.7447978416
C53	2.8921799307	-1.2582555091	2.9103443013
H54	3.5858540333	-0.7334340356	3.5714691448
H55	3.1997389482	-2.3015789678	2.7991273718
H56	-4.6822905005	-0.9646841144	-2.2721202286
H57	-5.0802656875	0.7455810202	-1.9439854940

C58	1.1204861040	1.4186711823	-2.1411337415
O59	0.5758869011	2.3905644998	-1.5199671636
C60	0.0079906394	-3.1002106337	-0.2078884962
O61	0.5721060557	-3.2456511426	0.8747961675
C62	-3.6608324828	4.6963144384	1.1837266834
C63	-2.6673599544	4.9505706412	0.2287885890
C64	-1.5577661955	4.1022596131	0.1677247865
C65	-1.4239498175	3.0071201410	1.0370337764
C66	-2.4315252736	2.7905576497	1.9866040196
C67	-3.5539616567	3.6229829036	2.0724675987
H68	-4.5271856805	5.3537527118	1.2418096266
H69	-0.7800252458	4.2918031848	-0.5677840199
H70	-2.3331186384	1.9638951173	2.6857081179
C71	-2.8082123809	6.1120492316	-0.7306040370
H72	-1.8374322713	6.4210418236	-1.1293996895
H73	-3.4435493534	5.8491192364	-1.5865914872
H74	-3.2672510126	6.9799547765	-0.2452724759
C75	-4.6049976501	3.3835884895	3.1341065824
H76	-4.3131259916	3.8323375583	4.0929014605
H77	-5.5683418748	3.8200994043	2.8512690593
H78	-4.7557872486	2.3135840002	3.3115487642

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Ir1	-0.4893922252	-1.6308293966	1.3466714295
C2	0.3058607865	-2.8830577841	3.8055650045
O3	1.0722828754	-3.5546066636	4.6816401018
N4	0.8384505138	-2.6363569994	2.6347463766
C5	-3.6921668496	-1.5087674556	4.0826119382
C6	-3.1684015500	-2.1335369116	5.2302669022
C7	-1.8459036811	-2.6123805579	5.2175308791
C8	-1.0478685119	-2.4457757642	4.0798718636
C9	-1.5656547916	-1.8014337756	2.9401644910
C10	-2.8963051949	-1.3413176345	2.9444841219
C11	-3.2159420900	-0.7893399516	1.6410213374
N12	-2.3006664839	-0.7775946840	0.7061693714
O13	-4.4220257018	-0.3026454984	1.3089314210
C14	2.5669906706	-3.9287858924	1.3960431617
H15	-4.7222720380	-1.1604660785	4.0858607231
H16	-1.4484766747	-3.1153377425	6.0962593023
H17	3.5822627818	-4.3365784043	1.4555506522
H18	2.4964130694	-3.2957646001	0.5080733102
C19	-2.6816417805	-1.0764807407	-1.7286367882
O20	0.5498792473	-2.0240116989	-0.6963467142
H21	1.8600968474	-4.7563568390	1.2862427697
H22	-3.0810614012	-2.0739040172	-1.5243624197
H23	-1.6187563011	-1.1687009029	-1.9635241976
H24	-3.1956542497	-0.6612838514	-2.6029437545
C25	0.2406613872	-4.0490470148	-1.9752730495

H26	0.5188541436	-3.4556871153	-2.8487501142
H27	1.0790156381	-4.7132944206	-1.7347842389
H28	-0.6294258342	-4.6709409710	-2.1957160686
C29	-4.0175027930	-2.2712220254	6.4751700433
H30	-3.7203731235	-3.1417929486	7.0681431102
H31	-3.9253009525	-1.3899941604	7.1230785183
H32	-5.0779956827	-2.3805538614	6.2269339188
C33	2.2487189930	-3.1095005446	2.6479407306
C34	-2.8678866193	-0.1547459407	-0.5195167516
C35	3.1946807869	-1.9047267021	2.7837507463
H36	3.0642195327	-1.2125888635	1.9490211395
H37	2.9995115355	-1.3582121985	3.7120702613
H38	4.2372260515	-2.2425191398	2.7952460479
C39	-2.2093904183	1.2093724737	-0.7664589104
H40	-2.6426622231	1.6788168472	-1.6571834641
H41	-2.3573735354	1.8789757422	0.0859116449
H42	-1.1342339239	1.0944797986	-0.9190401596
C43	-4.3671735500	-0.0120524973	-0.1160011996
C44	2.2503909453	-3.9754621949	3.9387289828
H45	3.1231639258	-3.8138240823	4.5746071101
H46	2.1434370819	-5.0449018183	3.7248518261
H47	-5.0115648342	-0.7362968741	-0.6254160596
H48	-4.7617491238	0.9955324683	-0.2664625918
C49	-0.0366268774	-3.1504675110	-0.7897253137
O50	-0.8351401850	-3.5338953623	0.1216679679

C51	0.1242119395	0.2194937724	2.1443986613
H52	-0.7374086754	0.7294535635	2.5934589582
H53	0.8044312019	-0.0101188960	2.9760073948
C54	2.0995368591	3.0718547306	-0.4372616546
C55	2.4337271742	1.7197955877	-0.5457944906
C56	1.7802847794	0.7911087217	0.2760678497
C57	0.8055402261	1.1858148978	1.2025749631
C58	0.4939812915	2.5554675981	1.2768115990
C59	1.1291938325	3.5062605279	0.4750604093
H60	2.5957669383	3.7998030723	-1.0776341605
H61	2.0037327191	-0.2644651406	0.1560670819
H62	-0.2624816507	2.8837942200	1.9882386148
C63	3.4904309664	1.2572297677	-1.5246342258
H64	3.1963830610	0.3223422353	-2.0132943196
H65	3.6728878166	2.0057024990	-2.3021537737
H66	4.4476355368	1.0706813643	-1.0199843264
C67	0.7945905708	4.9764424426	0.5961862487
H68	-0.1529219877	5.1298453398	1.1216433586
H69	1.5697212960	5.5179725979	1.1537044625
H70	0.7164953205	5.4534782285	-0.3872258029

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Ir1	0.8521382517	-3.9713577313	-1.5407778182

C2	-1.8340848410	-5.0156251263	-1.8628129475
O3	-3.0917109069	-5.1350317480	-2.2863463257
N4	-1.1216225775	-4.0603702081	-2.3950387750
C5	0.2428368470	-7.2130535927	1.1167935185
C6	-1.0761577505	-7.6265556263	0.8425494273
C7	-1.8337291309	-6.9543805341	-0.1330181820
C8	-1.2626244274	-5.8928053443	-0.8462315310
C9	0.0450680647	-5.5145734450	-0.5789061263
C10	0.8006726994	-6.1502123806	0.4025902666
C11	2.0989781971	-5.4948998104	0.5367674063
N12	2.3977507656	-4.4850300451	-0.2324449246
O13	3.0218700854	-5.8606290095	1.4160449900
C14	-1.9033637178	-1.8735404689	-3.3178194886
H15	0.8134699667	-7.7142586691	1.8943127797
H16	-2.8596581341	-7.2584137858	-0.3238540060
H17	-2.6383236884	-1.4269263363	-3.9977248243
H18	-0.9139455642	-1.4976203858	-3.5816933715
C19	3.6065561170	-2.5166489718	0.6517298395
O20	1.9113631089	-2.1880928653	-2.1622820148
O21	0.5936791543	-3.3843197431	1.8463795096
H22	-2.1423599408	-1.5769764247	-2.2925821263
H23	2.9351357535	-2.4903825291	1.5133053414
H24	3.1998008612	-1.8753209904	-0.1334939797
H25	4.5930263720	-2.1414114845	0.9478105344
C26	2.8009620464	-0.4916702804	-3.5482084501

H27	2.6355710393	0.2426279256	-2.7543761500
H28	3.8441190628	-0.8188883701	-3.4774506565
H29	2.6354846447	-0.0333820624	-4.5242987118
C30	-0.8476255441	-1.4650313974	1.6615383586
H31	-0.8231745777	-1.4771089679	2.7521560931
H32	-0.4453927097	-0.5162748317	1.2921092918
H33	-1.8823357040	-1.5354230634	1.3116655621
C34	-1.6696759048	-8.7965154665	1.5954076069
H35	-2.7624502674	-8.7528055108	1.6043042398
H36	-1.3831141555	-9.7505395499	1.1352697662
H37	-1.3241364069	-8.8195330291	2.6334814481
C38	-1.9292002764	-3.3957215893	-3.4623987630
C39	3.7365276292	-3.9492862487	0.1187620115
C40	-1.4109882050	-3.8539442675	-4.8332284779
H41	-0.3697336244	-3.5481817999	-4.9459334854
H42	-1.4868953957	-4.9423609113	-4.9336778201
H43	-2.0072933737	-3.3902238112	-5.6274211859
C44	4.6563190986	-4.0133514812	-1.1061153666
H45	5.6606178400	-3.6634016966	-0.8427221397
H46	4.7311455199	-5.0350419606	-1.4915370422
H47	4.2551359328	-3.3725269309	-1.8942727092
C48	4.1584415804	-4.9561027193	1.2373544147
C49	-3.3353427772	-3.9819458166	-3.1515349351
H50	-3.8644905166	-4.3390029971	-4.0364948756
H51	-3.9698592818	-3.2874024849	-2.5913149422

H52	4.3404470410	-4.4739442412	2.1999183124
H53	5.0185753692	-5.5712912201	0.9599848223
C54	1.8731045593	-1.6921423199	-3.3660641465
O55	1.1899756263	-2.1071901498	-4.3040454131
C56	-0.0254162202	-2.6229569067	1.1064980323
O57	-0.0696952952	-2.6741047351	-0.2051043196
O58	1.5664652097	-4.9611956668	-2.8663528984

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Ir1	0.9609342496	-4.0833143930	-1.3509808790
C2	-1.5898080864	-5.3685848196	-1.8815939846
O3	-2.7661478955	-5.6521344276	-2.4427526924
N4	-0.9181336825	-4.3708590751	-2.3872581683
C5	0.3140117834	-7.1829256582	1.4497703763
C6	-0.9296466320	-7.7250095981	1.0715313809
C7	-1.6216642873	-7.1839699484	-0.0281235049
C8	-1.0595522314	-6.1267089845	-0.7535413648
C9	0.1828134765	-5.6163552721	-0.3866484559
C10	0.8680857490	-6.1308033399	0.7166477197
C11	2.0960159855	-5.3788379324	0.9239969401
N12	2.4007961257	-4.4080431807	0.1037873534
O13	2.9558407870	-5.6107394662	1.9088044301
C14	-1.8328092632	-2.3352790179	-3.5043293679

H15	0.8294900876	-7.5774589228	2.3220671602
H16	-2.5936614208	-7.5855795381	-0.3036940704
H17	-2.4881983724	-2.0022385827	-4.3178381651
H18	-0.8632063905	-1.8472990585	-3.6155817967
C19	3.3441762799	-2.3210483796	1.0214786469
O20	2.0406571019	-2.3141315872	-2.0262866910
O21	0.2230169480	-3.4005167902	1.8916232979
H22	-2.2815570140	-2.0451527967	-2.5495533244
H23	2.5986773540	-2.3392494934	1.8207159460
H24	2.9514616261	-1.7411854345	0.1830957789
H25	4.2595154921	-1.8442386485	1.3907805471
C26	2.9162419941	-0.5465410173	-3.3288095480
H27	2.6443954167	0.2094024082	-2.5846626316
H28	3.9534225460	-0.8369427689	-3.1306309021
H29	2.8418977977	-0.1192973402	-4.3300868673
C30	-1.2489155022	-1.5480181357	1.4492824697
H31	-1.3928569066	-1.5464425816	2.5306912815
H32	-0.8465680274	-0.5830204195	1.1259221500
H33	-2.2121536811	-1.6812228864	0.9466483677
C34	-1.5107480227	-8.8878263294	1.8454805811
H35	-2.5894553808	-8.9736613655	1.6878550122
H36	-1.0574910569	-9.8385754814	1.5373188526
H37	-1.3351356234	-8.7790216575	2.9204909192
C38	-1.6527517964	-3.8522386926	-3.5798374675
C39	3.6567040416	-3.7457561494	0.5436860024

C40	-0.9019202979	-4.2797824622	-4.8487784483
H41	0.0947359280	-3.8354846040	-4.8428824373
H42	-0.8200040574	-5.3712554893	-4.9019031548
H43	-1.4444297649	-3.9294251416	-5.7345238266
C44	4.6803927791	-3.7457810772	-0.5966853744
H45	5.6160647267	-3.2851854667	-0.2594006149
H46	4.8928963001	-4.7639839766	-0.9365646764
H47	4.2814353906	-3.1695781893	-1.4342499458
C48	4.0744815808	-4.6863575879	1.7177865637
C49	-3.0085683954	-4.6018715065	-3.4288069043
H50	-3.3435853464	-5.0845538829	-4.3488316227
H51	-3.8052256275	-3.9643379414	-3.0320943969
H52	4.2223595308	-4.1582581535	2.6618816003
H53	4.9528358052	-5.2942954353	1.4837083151
C54	1.9937876825	-1.7608121827	-3.2003661081
O55	1.2983755437	-2.1173319143	-4.1553361112
C56	-0.2937486340	-2.6675096970	1.0525608641
O57	-0.1039747842	-2.7127572350	-0.2487152955
O58	1.8588566864	-5.0918152944	-2.6601741427
H59	2.0962431580	-6.2546921915	-2.4633689445
C60	2.3688523250	-7.5857753261	-2.4743383935
H62	1.4569183698	-8.0336070008	-2.0786321804
H63	2.4562437788	-7.6859138548	-3.5579122385
C63	5.9421396933	-8.2419667078	-0.2406697444
C64	6.0325738727	-7.7686101610	-1.5616977073

C65	4.8566685075	-7.5730047773	-2.2807742669
C66	3.5905564218	-7.8446892258	-1.7138623520
C67	3.5434215771	-8.3239866536	-0.3914844111
C68	4.7083124086	-8.5251158450	0.3557001503
H69	6.8560902420	-8.3931635750	0.3315114321
H71	4.9054737814	-7.1971139902	-3.3003249861
H72	2.5761461020	-8.5384076903	0.0564524822
C73	7.3853708205	-7.4940803108	-2.1789591754
H74	7.2950135420	-6.9144951175	-3.1015359245
H75	8.0315828045	-6.9368727275	-1.4916942028
H76	7.9064713020	-8.4278242770	-2.4231529889
C76	4.6276755974	-9.0241077700	1.7811951827
H77	4.1555365684	-10.0119579603	1.8336326780
H78	5.6200807560	-9.1059904429	2.2340477412
H79	4.0305583662	-8.3443829496	2.3998108743

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Ir1	0.7597493157	-3.9087688167	-1.4264737580
C2	-1.8478094065	-5.0252876606	-1.8263143090
O3	-3.1034324790	-5.1249748514	-2.2737813591
N4	-1.1397840082	-4.0365531618	-2.3008262645
C5	0.3060437737	-7.3076609906	1.0363804271
C6	-0.9906803424	-7.7607826230	0.7265538215

C7	-1.7707114732	-7.0600482301	-0.2112383044
C8	-1.2522762430	-5.9259859910	-0.8475595099
C9	0.0422525414	-5.4886742624	-0.5412763350
C10	0.8214116759	-6.1743235395	0.3996903714
C11	2.0976279458	-5.4908744914	0.5608555366
N12	2.3692585930	-4.4496134020	-0.1830963469
O13	3.0305048297	-5.8491801112	1.4438633732
C14	-1.9505576954	-1.7785564400	-2.9131228614
H15	0.8985553093	-7.8398089963	1.7765850334
H16	-2.7771723753	-7.4040173698	-0.4354754464
H17	-2.6280543893	-1.2301080508	-3.5769403127
H18	-0.9458807965	-1.3618021179	-3.0192471390
C19	3.6997207239	-2.4423857322	0.4403349812
O20	1.5725690688	-2.0752860380	-2.4254072091
O21	0.6639180909	-3.1537087575	1.8861822012
H22	-2.2649916208	-1.6313357422	-1.8766996228
H23	2.9770951759	-2.2183708078	1.2280890532
H24	3.4173041067	-1.8877002097	-0.4583464190
H25	4.6921879789	-2.1031509705	0.7575279797
C26	2.8089267166	-0.7350485014	-3.9167397490
F27	1.7682646142	0.0899363219	-4.1446414284
F28	3.5774235464	-0.1805023421	-2.9549893703
F29	3.5367950726	-0.8068850992	-5.0383856778
C30	-0.8575252088	-1.3043878301	1.6366218922
F31	-0.9267201443	-1.3083632985	2.9745757251

F32	-0.3160279437	-0.1300586894	1.2511290374
F33	-2.1208539334	-1.3494944701	1.1576534177
C34	-1.5344928385	-9.0080679093	1.3889359213
H35	-2.6283053958	-9.0076105197	1.4034167751
H36	-1.2151363023	-9.9143250146	0.8584888478
H37	-1.1849075086	-9.0968352957	2.4222254014
C38	-1.9481268461	-3.2670228851	-3.2771260975
C39	3.7261659407	-3.9464406824	0.1571311579
C40	-1.3950096780	-3.5048104122	-4.6912276597
H41	-0.3570132178	-3.1691730516	-4.7591801431
H42	-1.4262726478	-4.5680006128	-4.9506578294
H43	-1.9847783358	-2.9488072563	-5.4281698474
C44	4.6890503146	-4.2902509216	-0.9923040380
H45	5.6979691654	-3.9275168246	-0.7694097017
H46	4.7459324409	-5.3747509711	-1.1443763817
H47	4.3604775043	-3.8251486698	-1.9261784317
C48	4.0297011044	-4.7832413668	1.4338667644
C49	-3.3448670425	-3.9319889875	-3.0827268481
H50	-3.8089488393	-4.2551387972	-4.0166766807
H51	-4.0395469618	-3.2967079291	-2.5249797274
H52	3.8953288749	-4.2068038632	2.3532068674
H53	5.0144242059	-5.2546978135	1.4272526642
C54	2.3066231162	-2.1226016559	-3.4486181379
O55	2.6802739328	-3.1261514078	-4.1034937424
C56	-0.0066709303	-2.4926552010	1.1089069590

O57	-0.1435749564	-2.5785421793	-0.1744666978
O58	1.6177497122	-5.1019945186	-2.9843746255
H59	2.1085088607	-4.3668865420	-3.5358965038
H60	2.2969370208	-5.6735841018	-2.5981929129

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Ir1	-0.3551995881	-1.2496868416	1.6178718476
C2	0.2745958508	-3.1729812088	3.6316962936
O3	1.0099254996	-3.9481316116	4.4327298377
N4	0.9269480738	-2.4225358113	2.7857542784
C5	-3.9268245704	-2.6232145572	3.3337749726
C6	-3.4863623913	-3.5583823312	4.2885051227
C7	-2.1096865978	-3.8025703703	4.4454781859
C8	-1.1794099509	-3.1150983736	3.6585824643
C9	-1.6331739462	-2.1913672357	2.7096256643
C10	-2.9995035506	-1.9356194736	2.5432258048
C11	-3.1887015605	-0.9250816331	1.5127759185
N12	-2.1458439723	-0.4456960539	0.8914279569
O13	-4.3759943566	-0.4260294480	1.1620358568
C14	3.0894115581	-2.9339453741	1.6810196612
H15	-4.9912585217	-2.4362256488	3.2151209741
H16	-1.7727356360	-4.5261929905	5.1834237397
H17	4.1510827260	-3.1357289861	1.8601118447

H18	3.0128933952	-2.0963474394	0.9828707736
C19	-2.0929006818	0.3051669367	-1.4674702763
O20	-0.3974633429	0.2093770709	3.0898836344
O24	1.0772300019	-1.0475155179	-0.5132360699
H25	2.6405806514	-3.8151058787	1.2124407569
H26	-2.4655819416	-0.6699344976	-1.7962477295
H27	-1.0004628456	0.2894984283	-1.5033032923
H28	-2.4490827743	1.0689639617	-2.1671662287
C34	0.2221929511	2.2985460956	3.9668603090
F35	-1.0201140528	2.8308059469	3.8912260211
F36	0.3757010131	1.7917343539	5.2069716895
F37	1.1047917615	3.2926197688	3.8130252362
C41	0.9053694204	-2.9981373429	-1.9505231986
F42	1.7098848295	-2.3336865522	-2.7870423117
F43	1.5359850337	-4.1290259468	-1.5680827924
F44	-0.2075053705	-3.3491152164	-2.6219712706
C45	-4.4894572536	-4.2755611371	5.1652336811
H46	-4.1234427127	-5.2611439566	5.4678845412
H47	-4.6939953789	-3.7076046638	6.0813750849
H48	-5.4439712156	-4.4151308757	4.6488829039
C49	2.3873984516	-2.5877173297	2.9983957673
C50	-2.5689542898	0.6244766277	-0.0454929637
C51	2.9609424179	-1.3009294879	3.6107361459
H52	2.8190321395	-0.4589777775	2.9282634590
H53	2.4652935183	-1.0639777053	4.5576021750

H54	4.0335886191	-1.4195799235	3.7995967637
C55	-2.0146778517	1.9748131252	0.4318856795
H56	-2.3709999266	2.7788228886	-0.2214526158
H57	-2.3273388001	2.1921313952	1.4575605479
H58	-0.9216774990	1.9678991037	0.4043080526
C59	-4.1226394532	0.5369603375	0.0929713468
C60	2.3977061557	-3.7767396130	4.0084509967
H61	2.9932181834	-3.5818263716	4.9025104384
H62	2.7164031948	-4.7181684330	3.5506914587
H63	-4.6092165549	0.1569210865	-0.8098099968
H64	-4.5833815475	1.4823224226	0.3879268735
C62	0.4006139092	1.2048359473	2.8847802183
O63	1.2003812794	1.3530602792	1.9702397832
C61	0.5529940415	-2.1534443264	-0.7117887738
O62	-0.2874353283	-2.6931818895	0.0915930844

TS1-OCOCF$_3$

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Ir1	-0.2465769863	-0.0379154594	0.0852290379
C2	0.7502660868	-0.9329797668	2.6218177317
O3	1.6241025841	-1.3267219777	3.5498835821
N4	1.2458260129	-0.5186883167	1.4880414217
C5	-3.4890639304	-1.0659346368	2.5831798808
C6	-2.8649896413	-1.4600642168	3.7811373779

C7	-1.4614106375	-1.4235345727	3.8816817116
C8	-0.6939903803	-0.9699731480	2.8038045259
C9	-1.3259823233	-0.5461220046	1.6293862896
C10	-2.7169086495	-0.6082722088	1.5085162068
C11	-3.1115795968	-0.2113245909	0.1644061780
N12	-2.2063925441	0.1700873808	-0.6962601706
O13	-4.3733160081	-0.2622161093	-0.2679388538
C14	3.2932048009	-1.3728982905	0.3685832170
H15	-4.5707114526	-1.1303671607	2.4929309158
H16	-0.9782096639	-1.7670412697	4.7929753397
H17	4.3826620298	-1.4526392294	0.4561659388
H18	3.0574856984	-0.8717721575	-0.5739279064
C19	-2.3899021949	-0.7580616840	-2.9791934395
O20	0.9967517064	0.2332315729	-1.7978995095
H21	0.2489729556	1.8987899799	-0.2726703942
C22	-0.1785573649	2.0995939423	1.0909579113
H23	-0.0565585303	1.6174250531	2.0579674567
O24	-0.4348842403	-1.9397996078	-0.7298682286
H25	2.8592588936	-2.3746557342	0.3435101997
H26	-2.5888740722	-1.7483583287	-2.5623819850
H27	-1.3139966063	-0.6854427555	-3.1530545936
H28	-2.9086084848	-0.6609558180	-3.9398357993
H29	0.7073068679	2.7439972702	1.0095665856
C30	1.8726978991	1.7851366763	-3.4032411330
F31	2.6173349228	2.8954672479	-3.2990540379

F32	2.6560100183	0.7884173159	-3.8311436414
F33	0.9175558557	2.0039974731	-4.3337654521
C34	-0.4210609329	-4.2154478489	-1.2098646686
F35	-1.7430400908	-4.1828975469	-1.5029722662
F36	0.2548724954	-4.1078488693	-2.3729114163
F37	-0.1505911145	-5.4180765400	-0.6854272257
C38	-3.6961686790	-1.9235385449	4.9577594331
H39	-3.1792130531	-2.6999916697	5.5301405203
H40	-3.9085699134	-1.0973440729	5.6483812175
H41	-4.6575480668	-2.3310212340	4.6312844648
C42	2.7287118978	-0.5791848392	1.5502521663
C43	-2.8509779274	0.3551494981	-2.0263879672
C44	3.2928022461	0.8506214503	1.5900252169
H45	3.0201216885	1.3964314990	0.6822395884
H46	2.9046000214	1.4044015991	2.4513626405
H47	4.3858220161	0.8274247530	1.6583588656
C48	-2.5571212709	1.7418023812	-2.6089093147
H49	-3.1529008459	1.8936808667	-3.5163525545
H50	-2.8010142172	2.5288659338	-1.8908023240
H51	-1.5052986761	1.8429460792	-2.8845548782
C52	-4.3572416895	0.2168878132	-1.6441822542
C53	2.9333041438	-1.3216945675	2.9055467647
H54	3.6302558862	-0.8177794418	3.5787904165
H55	3.2324438205	-2.3645119948	2.7701489730
H56	-4.8930377965	-0.5133490351	-2.2545807143

H57	-4.8866864173	1.1743632890	-1.6623733668
C58	1.1870814133	1.4375367820	-2.0670242411
O59	0.8108067100	2.4189159049	-1.3614770613
C60	-0.0342223964	-3.0642114974	-0.2384973612
O61	0.5672641868	-3.3222810253	0.7935918701
C62	-3.7351152729	4.5379096473	1.0874312728
C63	-2.7300585439	4.7881048246	0.1423663786
C64	-1.5859845441	3.9864766853	0.1485314204
C65	-1.4262558690	2.9428640277	1.0765344187
C66	-2.4398455132	2.7369332113	2.0194598270
C67	-3.6011524111	3.5212939947	2.0351354262
H68	-4.6315123234	5.1561669225	1.0905372568
H69	-0.8011807188	4.1750403048	-0.5794377621
H70	-2.3222539552	1.9548146066	2.7651884602
C71	-2.8972474254	5.8953180070	-0.8742468802
H72	-1.9433550637	6.1578283605	-1.3402234294
H73	-3.5849522075	5.5995857965	-1.6769412083
H74	-3.3111976613	6.8001096667	-0.4161332482
C75	-4.6678766620	3.2822692444	3.0802046375
H76	-4.3693546592	3.6884844351	4.0549210388
H77	-5.6141699614	3.7564562422	2.8033459151
H78	-4.8537940274	2.2121080295	3.2219096366

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Ir1	0.0339691014	-1.5296695521	1.4646348590
C2	1.8081008945	-2.5212275307	3.4887167563
O3	2.9361215196	-2.9987674556	4.0381370992
N4	1.8418492983	-2.3003759017	2.1971346139
C5	-2.0027886036	-1.6963131644	5.1510177783
C6	-1.0179253365	-2.1574418542	6.0476223463
C7	0.2727590751	-2.4472713591	5.5739622404
C8	0.5817472540	-2.2717403327	4.2185731414
C9	-0.3997536660	-1.8006245774	3.3257724326
C10	-1.6964839653	-1.5179392081	3.7997202662
C11	-2.5250740530	-1.0833177116	2.6931091983
N12	-2.0078068904	-1.0106067949	1.4914402560
O13	-3.8286916780	-0.7836198957	2.7989473823
C14	2.9529979108	-4.1453231179	0.9867899571
H15	-3.0041317797	-1.4815722348	5.5180674988
H16	1.0293643062	-2.8103453751	6.2656323453
H17	3.9176086303	-4.5278346301	0.6346376029
H18	2.2771524869	-4.0754132538	0.1330349194
C19	-3.5616177698	-2.1393278403	-0.0672671555
O20	0.4644418027	-1.5396407826	-0.8225349607
H21	2.5291517496	-4.8699176826	1.6894896906
H22	-3.8689184649	-2.8305503908	0.7244760354
H23	-2.7515360777	-2.6115383782	-0.6243866650
H24	-4.4111975957	-1.9905026937	-0.7434878880

C25	0.0574060423	-3.4303698909	-2.2743426296
F26	0.5145386653	-2.6378488349	-3.2527765992
F27	0.8448145388	-4.5258419087	-2.2228409620
F28	-1.1877764050	-3.8293401092	-2.6068291029
C29	-1.3518736662	-2.3186235731	7.5150375221
H30	-0.5986187493	-2.9202188373	8.0317215777
H31	-1.4025920369	-1.3481006530	8.0247574414
H32	-2.3224998913	-2.8065515373	7.6550233475
C33	3.1470504913	-2.7788805063	1.6674999056
C34	-3.1264357503	-0.7868328183	0.5275674824
C35	3.7596175998	-1.7536201970	0.7121809022
H36	3.1064560608	-1.6122233605	-0.1532998991
H37	3.8875117953	-0.7856368671	1.2062267401
H38	4.7376099665	-2.0966654175	0.3573068618
C39	-2.7462088792	0.2107660027	-0.5635889095
H40	-3.5910819776	0.3706646975	-1.2424437973
H41	-2.4524615800	1.1689903674	-0.1294871070
H42	-1.9037760879	-0.1730010191	-1.1457530232
C43	-4.2060651734	-0.2456258743	1.4967477345
C44	3.9471374288	-2.9267088254	2.9907211029
H45	4.5774439453	-2.0546396243	3.1991907457
H46	4.5472724695	-3.8366931955	3.0441225927
H47	-5.2168647839	-0.5913928918	1.2742498054
H48	-4.1879579020	0.8473085074	1.5738488443
C49	0.0441000208	-2.7248031315	-0.9064130791

O50	-0.3928013845	-3.3863552446	0.0726868329
C51	0.8050838743	0.3642305355	1.9666353375
H52	1.5250474860	0.2169302349	2.7796544705
H53	1.3683508391	0.6141233274	1.0578509807
C54	-1.8495379023	3.6078909238	2.9621592907
C55	-1.4003191323	3.4640696148	1.6418124109
C56	-0.5436432330	2.4028787976	1.3391033249
C57	-0.1265845385	1.4845771904	2.3179804476
C58	-0.5775426661	1.6759110625	3.6307579008
C59	-1.4415126296	2.7256671852	3.9667170431
H60	-2.5170330452	4.4309984139	3.2129844315
H61	-0.1779701266	2.2854982262	0.3206384448
H62	-0.2454511888	0.9935937285	4.4100013570
C63	-1.8468726962	4.4364285289	0.5724317587
H64	-1.2421174106	4.3394546808	-0.3338768741
H65	-2.8941508230	4.2688402622	0.2896075598
H66	-1.7725888387	5.4735546983	0.9178343594
C67	-1.8961026438	2.9123784371	5.3971903371
H68	-2.1847708037	1.9581092528	5.8512821276
H69	-1.0955352728	3.3343418644	6.0180027153
H70	-2.7526528479	3.5902296350	5.4611755523

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Ir1	0.8493085013	-4.0014578085	-1.5638033825
C2	-1.8329957409	-5.0470953422	-1.8474548677
O3	-3.1026185753	-5.1366266510	-2.2267870574
N4	-1.1195517459	-4.1001640021	-2.3944236584
C5	0.2765770463	-7.1950114820	1.1481629060
C6	-1.0383070331	-7.6258521704	0.8821678779
C7	-1.8052301305	-6.9763713802	-0.1026715163
C8	-1.2454468568	-5.9236716220	-0.8371585527
C9	0.0606334148	-5.5340009951	-0.5786864930
C10	0.8243632922	-6.1398601104	0.4142906508
C11	2.1151826409	-5.4663989735	0.5412658971
N12	2.3998231311	-4.4577305617	-0.2369843429
O13	3.0394570026	-5.8116721010	1.4230030686
C14	-1.9289835707	-1.8564364564	-3.1046716080
H15	0.8523671383	-7.6753777768	1.9346579068
H16	-2.8304601940	-7.2891696463	-0.2815464114
H17	-2.6746394197	-1.3525777963	-3.7297955822
H18	-0.9469513611	-1.4513414828	-3.3533861993
C19	3.6069568736	-2.4672485248	0.6173079233
O20	1.9192268392	-2.2241567456	-2.1996529333
O24	0.4798369302	-3.2880745962	1.8565950094
H25	-2.1457574434	-1.6507566149	-2.0529766719
H26	2.9246969965	-2.4257273711	1.4702102150
H27	3.2246593169	-1.8216022396	-0.1760681787
H28	4.5904733016	-2.0971506485	0.9279219677

C34	3.0196255218	-0.6106802413	-3.4862782163
F35	2.9875428436	0.2424480462	-2.4425064949
F36	4.2431242563	-1.1991175480	-3.4889847641
F37	2.9095600093	0.1060023078	-4.6109739242
C41	-1.0500915513	-1.4635533808	1.4938444103
F42	-1.2578149091	-1.5006578034	2.8160419893
F43	-0.5230315996	-0.2630700927	1.1850896494
F44	-2.2552820874	-1.5520443268	0.8831656405
C45	-1.6196627395	-8.7878699175	1.6555826297
H46	-2.7113553487	-8.7369131914	1.6930018293
H47	-1.3509603847	-9.7446139483	1.1905800287
H48	-1.2462090130	-8.8088757207	2.6836614395
C49	-1.9580552209	-3.3610965241	-3.3849463738
C50	3.7397803801	-3.9062790258	0.1016139105
C51	-1.4775665973	-3.6968682058	-4.8027783750
H52	-0.4482909053	-3.3587544707	-4.9329770738
H53	-1.5335578261	-4.7751358924	-4.9880194660
H54	-2.1106499258	-3.1860773306	-5.5368301156
C55	4.6658911682	-3.9852534039	-1.1182888756
H56	5.6799040558	-3.6835905787	-0.8332609875
H57	4.7057421084	-5.0032421894	-1.5188646916
H58	4.3156889908	-3.3106726447	-1.9016153889
C59	4.1685977454	-4.8962896333	1.2337933043
C60	-3.3575545691	-3.9780504210	-3.0853838333
H61	-3.8723483795	-4.3388694496	-3.9772862875

H62	-4.0097270076	-3.3028218746	-2.5238886666
H63	4.3436303459	-4.4017063579	2.1911324039
H64	5.0338458369	-5.5073468827	0.9649040884
C62	1.9159439512	-1.6987037843	-3.3735484529
O63	1.2214688839	-1.9504825396	-4.3484313888
C61	-0.1096743631	-2.6097625794	1.0306086538
O62	-0.0862689351	-2.6654654261	-0.2626071798
O58	1.5690037243	-4.9947915088	-2.8753249456

TS2-$OCOCF_3$

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Ir1	1.1577515656	-4.0265756440	-1.5474099480
C2	-1.2171227436	-5.3483970133	-2.5440582874
O3	-2.3617311066	-5.5519931316	-3.1911926434
N4	-0.5887518237	-4.2327579027	-2.7887715389
C5	0.6215565655	-7.6891425245	0.4924703700
C6	-0.5371026178	-8.2267974760	-0.0941099910
C7	-1.1999949588	-7.5185679636	-1.1197464612
C8	-0.6880205072	-6.2986851606	-1.5658270875
C9	0.4739898323	-5.7886567054	-0.9915078352
C10	1.1256759178	-6.4623525279	0.0411453619
C11	2.2414355336	-5.6614442945	0.5266700160
N12	2.4965809007	-4.5084182879	-0.0338026331
O13	3.0343259170	-6.0222692503	1.5281804549

C14	-1.6414763967	-2.0411087872	-3.3119424746
H15	1.1092086919	-8.2180910640	1.3069718341
H16	-2.1142085782	-7.9220930928	-1.5479109078
H17	-2.3223090852	-1.5384399695	-4.0083588244
H18	-0.7150248533	-1.4665536411	-3.2644442089
C19	3.1525476200	-2.5425911682	1.3268451547
O20	2.0751673789	-2.0596916402	-1.7336185370
O21	0.0357900376	-4.0025994259	1.7273859421
H22	-2.0998810179	-2.0657632405	-2.3195643118
H23	2.3161005129	-2.7418647789	2.0018500303
H24	2.8335574747	-1.8308021633	0.5625421467
H25	3.9752442213	-2.0996473483	1.8997276055
C26	3.1333655893	-0.1285486936	-2.5130478469
F27	2.8459592678	0.5157983281	-1.3620842487
F28	4.4032931884	-0.5991240532	-2.4029939121
F29	3.1203384911	0.7718211594	-3.5038672287
C30	-1.6677507291	-2.3431013402	1.3436896016
F31	-2.0808169698	-2.6253742653	2.5860149511
F32	-1.3241494308	-1.0418519436	1.3016460691
F33	-2.7204531086	-2.5170524464	0.5094648463
C34	-1.0848262527	-9.5574185648	0.3719164432
H35	-2.1722561380	-9.5202385297	0.4929732968
H36	-0.8663891736	-10.3534842418	-0.3506284359
H37	-0.6499949891	-9.8539719603	1.3300033044
C38	-1.3485761816	-3.4576767726	-3.8137800443

C39	3.6302460433	-3.8415410371	0.6638987818
C40	-0.5597360290	-3.4522222617	-5.1296253017
H41	0.3971935413	-2.9493199391	-4.9812877332
H42	-0.3844154899	-4.4742858454	-5.4826272481
H43	-1.1264183672	-2.9120879572	-5.8965609776
C44	4.7758155582	-3.5793253950	-0.3210474643
H45	5.6370648895	-3.1638845528	0.2136025131
H46	5.0910522899	-4.5042801686	-0.8147960212
H47	4.4615189647	-2.8603882451	-1.0795959135
C48	3.9960923881	-4.9354574073	1.7192309313
C49	-2.6468157496	-4.3142197521	-3.9179879415
H50	-2.9050887708	-4.5878096141	-4.9426044688
H51	-3.5065918059	-3.8468283428	-3.4287410575
H52	3.8883116090	-4.5882823455	2.7489268418
H53	4.9932691438	-5.3585342558	1.5719416460
C54	2.1531460144	-1.3067256920	-2.7705263252
O55	1.6115609646	-1.4010952403	-3.8642353096
C56	-0.4767548667	-3.2454678109	0.9186624651
O57	-0.1872654414	-3.0302708589	-0.3255515540
O58	2.2724209043	-4.6626854709	-2.9114176990
H59	2.9080312644	-5.6912659045	-2.7412286861
C60	3.6875921923	-6.7822711318	-2.6728486555
H61	4.6578053225	-6.3212405415	-2.8673002316
H62	3.5726392932	-7.1169911539	-1.6418331915
C63	2.2449805143	-9.4337794740	-5.6736549668

C64	3.2180476067	-8.4815512428	-6.0139967270
C65	3.6870369738	-7.6264872638	-5.0194259003
C66	3.2080567932	-7.7070684800	-3.6948442172
C67	2.2241320215	-8.6715524538	-3.3937674518
C68	1.7398031133	-9.5412327713	-4.3700070662
H69	1.8708424656	-10.1066307522	-6.4436679746
H71	4.4377058187	-6.8782157966	-5.2630715689
H72	1.8407370016	-8.7356149271	-2.3775524340
C73	3.7278435942	-8.3875561058	-7.4338763349
H74	4.5667991364	-7.6911615341	-7.5130189215
H75	4.0625205158	-9.3634080753	-7.8032996153
H76	2.9413345515	-8.0387650652	-8.1137611930
C76	0.7106597545	-10.5964491304	-4.0331239516
H77	0.1704789607	-10.3470275553	-3.1149626699
H78	-0.0237182107	-10.7103924794	-4.8373951215
H79	1.1805976205	-11.5767985293	-3.8841325523

Table S22.Tabulated Data for DFT Calculations

Molecule	ZPE [kcal/mol]	Hvib	Svib	6kT	1/2 (Strans+S	Selec	Htot	Stot	G(solv)-benz	E(SCF, large	G (Acetonitrile	# basis
X = Oac												
1 (aquo)	305.066	19.212	127.9591447227	3.552756	40.5955	0	21.582	210.092	-1.52E-003	-1558.09243	-977442.361	913
1b	288.183	18.298	124.2945148744	3.552756	40.458	0	20.668	206.734	-4.67E-003	-1481.63749	-929484.792	877
TS1-OAc	401.202	24.73	167.9625249997	3.552756	41.43	0	27.1	252.914	4.79E-004	-1831.608	-1148985.29	
2	364.658	21.305	142.8489455255	3.552756	41.0695	0	23.675	227.287	-2.18E-004	-1602.60321	-1005315.39	
5-OAc	290.092	19.061	126.6378449139	3.552756	42.7565	2.183	21.431	210.048	-3.71E-003	-1556.78573	-976639.145	
TS2-OAc	401.786	25.808	176.2650723924	3.552756	44.414	2.813	28.178	264.406	-2.46E-003	-1906.76339	-1196149.57	
X = TFA												
3 (aquo) (ax or eq?) ax no	275.865	21.166	147.4775776945	3.552756	41.431	0	23.536	226.497	-3.24E-003	-2153.54847	-1351131.15	1003
3b (non aquo)	259.539	20.152	142.5161947419	3.552756	41.333	0	22.522	222.835	-2.49E-003	-2077.10159	-1303175.36	967
TS 1	372.43	27.202	188.1590112035	3.552756	42.0945	0	29.572	278.813	4.34E-004	-2427.07419	-1522678.6	
4	350.314	21.988	146.8873803544	3.552756	41.4755	0	24.358	234.059	7.61E-004	-1900.33517	-1192159.44	
5-OCOCF3	261.537	21.497	145.8965210671	3.552756	43.5855	2.183	23.867	234.483	-3.72E-003	-2152.25739	-1350335.46	
TS2-OCOCF3	373.111	28.356	197.6468307654	3.552756	44.481	2.183	30.726	291.642	-2.94E-003	-2502.21258	-1569832.48	
											-0.082844	
											-0.082844	
											-0.082844	
											-0.082844	
Small Molecules											G	
Water	13.413	0.002	0.006	3.552756	23.2415	0	2.372	46.49		-76.4182254	-47953.2891	36
Mesitylene	114.781	4.444	30.727	3.552756	34.7195	0	6.814	100.166		-349.998067	-219538.801	282
O2 Triplet	2.376	0.002	0.006	3.552756	25.5925	2.183	2.075	49.008		-150.291	-94319.4917	44
Oac	38.904	1.076	6.532	3.552756	31.028	0	3.446	68.589		-229.032	-143699.972	116
TFA	24.615	2.142	13.995	3.552756	33.6545	0	4.512	81.305		-526.753	-330538.529	161
3,5 dimethylbenzaldehyde	1.03E+002	4.503	29.186	3.552756	35.2455	0	6.873	99.678		-424.003203	-265986.814	
Electron	-71.7166	-71.7166		Potential	-1.17	V						
H+	-279.82	-279.82										
Conversion to Ag2O	1.38	1.38										

Free Energies	
Oac	G (benz)
1b	4.3
TS 1	42.6
2	12.5
11	12.4
TS 3	38.1
TFA	G (benz)
3b (non aquo)	2.5
TS 1	38.1
4	18.7
11	4.9
TS 3	46.7

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